INTERNATIONAL ATOMIC WEIGHTS

1943

Published by the Journal of the American Chemical Society

	Symbol	Atomic Number	Atomic Weight		Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	26 97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121 76	Neodymium	Nd	60	144 27
Argon	A	18	39 944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58 69
Barium	Ba	56	137 36	Nitrogen	N	7	14 008
Beryllium	Be	4	9 02	Osmium	Os	76	190 2
Bismuth	Bi	83	209 00	Oxygen	O	8	16 0000
Boron	B	5	10 82	Palladium	Pd	46	106 7
Bromine	Br	35	79 916	Phosphorus	P	15	30 98
Cadmium	Cd	48	112 41	Platinum	Pt	78	195 23
Calcium	Ca	20	40 08	Potassium	K	19	39 096
Carbon	C	6	12 010	Praseodymium	Pr	59	140 92
Cerium	Ce	58	140 13	Protactinium	Pa	91	231
Cesium	Cs	55	132 91	Radium	Ra	88	226 05
Chlorine	Cl	17	35 457	Radon	Rn	86	222
Chromium	Cr	24	52 01	Rhenium	Re	75	186 31
Cobalt	Co	27	58 94	Rhodium	Rh	45	102 91
Columbium	Cb	41	92 91	Rubidium	Rb	37	85 48
Copper	Cu	29	63 57	Ruthenium	Ru	44	101 7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150 43
Erbium	Er	68	167.2	Scandium	Sc	21	45 10
Europium	Eu	63	152 0	Selenium	Se	34	78 96
Fluorine	F	9	19 00	Silicon	Si	14	28 06
Gadolinium	Gd	64	156 9	Silver	Ag	47	107.880
Gallium	Ga	31	69 72	Sodium	Na	11	22 997
Germanium	Ge	32	72 60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32 06
Hafnium	Hf	72	178 6	Tantalum	Ta	73	180 88
Helium	He	2	4 003	Tellurium	Te	52	127.61
Holmium	Ho	67	164 94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204 39
Indium	In	49	114 76	Thorium	Th	90	232.12
Iodine	I	53	126 92	Thulium	Tm	69	169.4
Iridium	Ir	77	193 1	Tin	Sn	50	118.70
Iron	Fe	26	55 85	Titanium	Ti	22	47 90
Krypton	Kr	36	83 7	Tungsten	W	74	183.92
Lanthanum	La	57	138 92	Uranium	U	92	238.07
Lead	Pb	82	207 21	Vanadium	V	23	50.95
Lithium	Li	3	6 940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174 99	Ytterbium	Yb	70	173 04
Magnesium	Mg	12	24 32	Yttrium	Y	39	88.92
Manganese	Mn	25	54 93	Zinc	Zn	30	65 38
Mercury	Hg	80	200 61	Zirconium	Zr	40	91.22

STANDARD METHODS OF CHEMICAL ANALYSIS

A Manual of Analytical Methods and General Reference for the Analytical Chemist and for the Advanced Student

BY

WILFRED W. SCOTT, Sc.D.

Late Professor of Chemistry, University of Southern California. Author of "Qualitative Chemical Analysis," "Technical Methods of Metallurgical Analysis," "Inorganic Quantitative Chemical Analysis."

FIFTH EDITION

EDITED BY

N. HOWELL FURMAN, Ph.D.

Professor of Chemistry, Princeton University

IN COLLABORATION WITH EMINENT SPECIALISTS

IN TWO VOLUMES, ILLUSTRATED

VOLUME ONE—THE ELEMENTS

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PREFACE TO THE FIFTH EDITION

An extensive revision of "Standard Methods of Chemical Analysis" was in progress during the years 1930–2 and approximately half of the first volume was in galley proof when the work was interrupted by the death of Professor W. W. Scott. A further revision and extension of the book was undertaken in 1936 by the present editor in cooperation with the majority of the former collaborators, or their associates, and a number of new contributors.

As a result of this cooperation the book has undergone its most thorough revision as well as a very considerable expansion in content. Nearly all of the chapters that appeared in the fourth edition have been either drastically revised or entirely rewritten.

Among the chapters that have been entirely rewritten are those on Aluminum by H. V. Churchill, R. W. Bridges and the staff of the Analytical Laboratory of the Aluminum Company of America, which incorporate the standard methods of that company; Cadmium and Zinc by L. A. Wilson of the New Jersey Zinc Company; Cerium and other Rare Earths, Thorium, Zirconium and Hafnium by P. H. M-P. Brinton; Columbium, Tantalum, Gallium, Indium, Scandium and Thallium by W. R. Schoeller; Sodium, Potassium and the Other Alkali Metals by W. B. Hicks of the Solvay Process Company; Radium by L. D. Roberts; Reagents by N. H. Furman; Non-Ferrous Alloys by W. J. Brown of the National Lead Company; Bituminous Substances by H. A. Abraham of the Ruberoid Company; Soap Analysis by C. P. Long, incorporating the standard methods of the Procter and Gamble Company; Potentiometric Titration by N. H. Furman; and Gas Analysis by the late Professor A. H. Gill of the Massachusetts Institute of Technology.

The book contains new chapters on Rhenium by Loren C. Hurd; Ferrous Alloys based on the methods of the American Society for Testing Materials; Electrometric pH Measurement by W. N. Greer of the Leeds and Northrup Company; Colorimetric pH

Measurement by F. H. McCrumb and W. A. Taylor; Conductometric Titrations by I. M. Kolthoff; Chemical Microscopy by E. M. Chamot and C. W. Mason; Quantitative Microanalysis by L. T. Hallett; Analysis of Rubber Compounding Ingredients by R. B. Stringfield; Quantitative Spectrographic Analysis by W. R. Brode.

New material appears in almost every chapter. In addition to the vast amount of material that was collected by Professor Scott and by the present editor, specific contributions to individual chapters were added on: Alundum, and Boron Carbide by the Norton Company through M. O. Lamar; Beryllium-Copper Alloys by C. H. Davis of the American Brass Company; Boron by the Pacific Borax Company, by Mrs. S. K. Webb and others. The book also includes extensive contributions and revisions on Chromium, Manganese, Molybdenum, Tungsten and on other subjects by Thomas R. Cunningham in the form of standard methods of the Electrometallurgical Company; on Copper by Eugene Fitzpatrick of the Nichols Copper Company; on Iron and on Titanium by W. M. Thornton, Jr.; on Lead by A. J. Nicklay of the Eagle-Picher Company and J. R. Sheppard; and on Nickel by Calvin Sterling of the International Nickel Company. Methods of the American Cyanamid Company for hydrogen cyanide and other compounds were furnished by C. P. Davis. The chapter on Titanium was revised by J. L. Turner of the Titanium Division of the National Lead Company.

Extensive revision will also be found in the chapters on the Chemical and Bacteriological Examination of Water. The former was contributed by D. K. French and the latter by F. E. Hale. The section on Fuels was revised by incorporating methods from the American Society for Testing Materials, while the chapters on Explosives and Rubber were revised by their original authors, C. G. Storm and L. A. Salas.

Sundry contributions have been made by many other contributors, some of which are acknowledged here but all of which are acknowledged in the body of the text. These include a revision of the Solubility Tables by W. D. Leech; contributions to the sections on Magnesium Alloys and the analysis of Sodium Sulfide by A. W. Beshgetoor of the Dow Chemical Company; various

procedures were contributed by L. J. Stabler, R. H. Pierson, B. S. Taylor, G. Thorp, L. S. Bushnell, J. B. Chatelain, E. R. Caley, W. S. Allen, W. J. Boyer, L. E. Harper, E. P. Herner, C. H. McCollam, J. Strauss, and others.

Since the publication of the fourth edition have occurred the deaths of Professor Scott and four other major contributors, Dr. Victor Lenher, Dr. R. K. Meade, Dr. I. A. Palmer and Dr. A. H. Gill. Dr. Lenher's chapter on Selenium and Tellurium was originally revised by Professor Scott and later re-revised by Dr. W. R. Schoeller. Dr. Meade's chapter on Cement was revised by W. C. Hanna of the California Portland Cement Company. The revision of Professor Palmer's chapter on the Fire Assay is based on the detailed suggestions of T. A. Wright of the Lucius Pitkin Company. The present editor has undertaken the revision of the majority of the numerous chapters which were originally contributed by Professor Scott. Dr. Gill revised his chapters on Gas Analysis and on Oils, Fats and Waxes in 1936.

The editor received helpful collaboration from many sources and this is gratefully acknowledged here as well as in the body of the text. The editor also wishes to record his obligation to a number of individuals who gave general advice about numerous matters in either the earlier or the latter stages of the revision; T. R. Cunningham, I. M. Kolthoff, S. Skowronski, G. Frederick Smith, H. H. Willard, T. A. Wright, and the late Stephen Popoff. Advice on special procedures which is also gratefully acknowledged was received from W. H. Chapin, E. H. Mahin, W. M. Thornton, Jr., and the late S. W. Parr. The editor wishes also to acknowledge the valuable assistance of E. R. Caley and J. F. Flagg in reading the proof; of Mrs. A. Z. Muelken in the typing of the manuscript; and of his daughter Carol in preparing the Index.

Permission to reproduce material from various journals and books of standard methods was very generously granted by the American Chemical Society, the American Society for Testing Materials, the Technical Association of Pulp and Paper Industries and the Association of Official Agricultural Chemists.

Typographically the book is entirely new; complete resetting has made possible the use of more appropriate headings and a more pleasing type page. The publishers have spared neither effort

nor expense to improve the quality of the book; to this end they have sacrificed much material that was already in galley form in the progress of the revision of 1932.

The spirit of cooperation on the part of the various collaborators has been noteworthy. This is a tribute to the genius of Professor Scott in the early development of the project. On behalf of the various contributors and the hosts of friends of the earlier editions, the present editor expresses the hope that the fifth edition has preserved and enhanced those uniquely valuable qualities which made the work of such broad service to advanced students, professional analysts, and research workers in all fields of chemistry.

N. HOWELL FURMAN, *Editor.*

PRINCETON, N. J.,
June, 1938.

PREFACE TO FIRST EDITION

THIS book is a compilation of carefully selected methods of technical analysis that have proven of practical value to the professional chemist. The subjects have been presented with sufficient detail to enable one with an elementary knowledge of analytical processes to follow the directions; on the other hand, lengthy exposition, theoretical dissertation and experimental data are purposely avoided, in order to include a large amount of information in a compact, accessible form. References to original papers are given when deemed advisable.

For methodical arrangement the material is grouped under three major divisions—Part I. Quantitative determination of the elements. Part II. Special subjects. Part III. Tables of information.

In the first division the elements are generally taken up in their alphabetical order, each chapter being fairly complete in itself, cross-references being given to certain details included elsewhere to avoid repetition. For example, the complete directions for separation of the halogens are given in the chapter on chlorine, and references to these details are given in the chapters dealing with the other members of this group. Occasionally it has been deemed advisable to place several related elements together in the same chapter.

Each chapter on the elements is generally arranged according to the following outline:

Physical Properties. Atomic weight; specific gravity; melting-point; boiling-point; oxides.

Detection. Characteristic reactions leading to the recognition of the element.

Estimation. The subject is introduced with such information as is useful to the analyst.

Preparation and Solution of the Samples. Here directions are given for the preparation and decomposition of characteristic materials in which the element occurs. Recommendations to the best procedures are included to assist the analyst in his choice.

Separations. This section is devoted to procedures for the

removal of substances, commonly occurring with the element, that may interfere with its estimation. In the absence of such substances, or in case methods are to be followed by which a direct estimation of the element may be made in the presence of these substances, this section on separations may be omitted in the course of analysis. Here the discretion of the chemist is necessary, and some knowledge of the substance examined essential.

Methods. The procedures are grouped under gravimetric and volumetric methods. Several processes are generally given to afford the opportunity of selection for particular cases and for economical reasons where special reagents may not be available.

In many of the chapters methods for determining traces of the element are given, and the subjects are concluded by typical examples of complete analysis of substances containing the elements.

The titles to the procedures generally give a clue to the processes. Names of originators are occasionally retained where common usage makes the methods generally known by these.

Although the combined acid radicals are taken up with the elements to which they may be assigned, a chapter is devoted to the more important of the acids in their free state, and is placed with the other special subjects in the second division of the book. Here are found chapters on water, paint, oil, alloys, coal, cement, gas, and such subjects as are best classed in sections apart from simple substances dealt with in the first portion of the work.

The last portion of the book is devoted to tables of the more important arithmetical operations. These are designed to assist the analyst to greater accuracy of calculations, as well as to relieve him of needless expenditure of time and energy.

The material herein included has been carefully selected, an effort having been made to obtain the more trustworthy methods that will meet the general needs of technical chemists.

A list of the majority of publications consulted is given in alphabetical order in the appendix of this volume. Reference to these authorities will be found throughout the book.

W. W. SCOTT.

NEW YORK CITY,
January, 1917.

INTRODUCTION*

The fundamental importance of analytical chemistry is shown by the urgent demands on this branch of chemistry. Our present day knowledge of elements has been made possible by analysis. The separations in metallurgy are dependent upon analytical principles. Startling discoveries in medicine have been dependent on accurate analysis and the same is true in regard to experimental research, where analytical methods are employed for ascertaining the composition of the products formed. The importance of analysis for control of chemical industrial processes has created a demand for rapid methods so that there is a constant effort on the part of the analytical chemist to simplify procedures of analysis. On the other hand our extended knowledge of the nature of substances and their chemical reactions has shown errors in former methods of procedure and the necessity for modifications which are being developed to take care of interferences. This accounts for the large number of specialized methods that appear in chemical literature and the vast amount of work that has been done for coupling accuracy with simplicity, wherever this is possible. Research demands accuracy in analytical procedures with sacrifice of simplicity and rapidity, should these be impossible; on the other hand rapid methods are essential to the economic control of chemical industrial processes.

A correct evaluation of materials for one or more of the substances desired, necessitates careful sampling, for obtaining representative portions for analysis. Ores and minerals of uniform composition are exceptions; even in the case of alloys, where a uniform composition would be expected, segregation of elements of the molten mixtures during the process of cooling is known to take place. Sampling of solutions is no exception to the necessity of careful procedure. A chapter is devoted to the subject under the specialized section of this book—Volume 2.

An early training in the chemical laboratory, generally starting

*By W. W. Scott.

in the high school and carried on in the college or university, has acquainted the chemist with the common apparatus employed in the analytical laboratory. He is familiar with the different forms of containers—beakers, casseroles, flasks, crucibles—closed or perforated forms, made of porcelain, silica or other refractory materials, or of metals—iron, nickel, platinum and certain resistant alloys. The chemist is familiar with different types of measuring apparatus—the balance, burette, measuring flasks, pipettes etc. He has used different forms of heating or combustion apparatus—drying ovens, burners and furnaces. He has become familiar with laboratory operations and technique, details of which appear in elementary texts of analytical chemistry, used in his preparation for a professional career. It has been considered unnecessary to give such details here. Throughout the work attention is called to special apparatus and cautions in technique and operations where these are considered necessary. A chapter appears in the later portion of this volume on special apparatus and calibration methods that will be found useful.

In the preparation and decomposition of the material for analysis care must be exercised to avoid loss by volatilization or separation; for example the volatility of mercury compounds, silicon and fluorine in presence of each other during the acid attack, stannic chloride, boron in certain combinations; the precipitation of certain radicals with silica during the action of strong acids, and the co-precipitation of a number of substances with aluminum hydroxide (the ammonia precipitate). Throughout the text precautions are given to avoid such losses and attention is called to the steps where such losses are apt to occur. In the mechanical preparation of the material fine grinding of refractory substances is generally advisable. It must be remembered, however, that chemical changes may take place, for example oxidation of sulfide ores leading to low results. Then again contamination by abrasion of the grinding apparatus must be guarded against.

The amount of the sample required for analysis depends not only upon the percentage of the element or substance in the material, but also upon the delicacy of the method, that is to be used. In the determination of the more common elements in ores and minerals a 0.5 gram sample is generally sufficient. In micro-

methods, a few milligrams are sufficient, while in the determination of the so called "traces" of impurities much larger samples may be required.

In complete analysis of substances it may be advisable to take separate samples for individual estimations, as in case of carbon dioxide in carbonates, the estimation of carbon, fluorine, and chlorine. On the other hand combinations may be better, for example the determination of silica, titanium, manganese and nickel in the same sample; chromium and vanadium; barium and zirconium; iron, aluminum, titanium, vanadium, zirconium and the phosphate radical in the same sample. Procedures in the text indicate the best conditions for accuracy, and the operations necessary for removal of interfering substances.

In the manufacture of this book, the publishers have observed the recommendations of the War Production Board and any variation from previous printings of the same book is the result of this effort to conserve paper and other critical materials as an aid to the war effort.

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* Deceased.

CONTENTS

VOLUME I. PART I. THE ELEMENTS

ALUMINUM

ANTIMONY

ARSENIC

BARIUM

BERYLLIUM

BISMUTH

BORON

BROMINE

CADMIUM

CALCIUM

CARBON

CERIUM AND THE OTHER RARE-EARTHS

CHLORINE

CHROMIUM

COBALT

COLUMBIUM AND TANTALUM

COPPER

FLUORINE

GALLIUM

GERMANIUM

GOLD

HYDROGEN

INDIUM

IODINE

IRON

LEAD

MAGNESIUM

MANGANESE

MERCURY

MOLYBDENUM

PHOSPHORUS

PLATINUM METALS

Platinum, Palladium, Iridium, Ruthenium, Rhodium and Osmium

RADIUM

RHENIUM

SCANDIUM

SELENIUM AND TELLURIUM

SILICON

SILVER

THE FIRE ASSAY FOR GOLD AND SILVER

SODIUM AND THE OTHER ALKALI METALS

STRONTIUM

SULFUR

THALLIUM

THORIUM

TIN

TITANIUM

TUNGSTEN

URANIUM

VANADIUM

ZINC

ZIRCONIUM AND HAFNIUM

PART II. QUALITATIVE TESTS OF SUBSTANCES

PART III

TABLES AND USEFUL DATA

REAGENTS AND STANDARD SOLUTIONS

STANDARD LABORATORY APPARATUS

SOLUBILITY TABLE

INDEX

TABLE OF ATOMIC WEIGHTS

VOLUME I

PART I

METHODS FOR THE DETECTION AND DETERMINATION OF THE MORE IMPORTANT ELEMENTS

ALUMINUM *[1]

Al, *at.wt.* 26.97; *sp.gr.* 2.71; *m.p.* 658.7; *b.p.* 1800° C.; *oxide* Al_2O_3

Aluminum metal was first isolated by Oersted[2] 1825 by reduction of the chloride with potassium. The element stands next to oxygen and silicon in abundance and is estimated as comprising nearly eight per cent of the earth's solid shell. The element is not found free, but its compounds are numerous. It is found in all soils and in a large part of the rocks, limestone and sandstone being the only notable exceptions. It occurs in feldspar, granite, mica, mica schist, clay, obsidian, porphyry, slate, zeolite. The precious stones ruby, garnet, sapphire, topaz, turquoise, tourmalin are aluminum minerals. The commercial source of aluminum and its compounds is bauxite, an impure hydrated alumina—$Al_2O_3.XH_2O$. Titanium and vanadium are frequently present, a fact to be remembered in the aluminum determination. The minerals alunite, $K_2Al_6(OH)_{12}(SO_4)_4$; cryolite, Na_3AlF_6, and clay are other sources.

DETECTION

General Procedure.—The sample is prepared by one of the procedures outlined under "Preparation and Solution of the Sample." Silica is removed by taking the solution to dryness, boiling the residue with hydrochloric acid and

* *Chapter* contributed by H. V. Churchill, R. W. Bridges and Analytical Chemical Staff of the Aluminum Company of America.

[1] Although alum was recognized as a separate substance and manufactured from alum stone by the alchemists of the Middle Ages, the metal aluminum was unknown until it was discovered by Oersted 1825 by reduction of aluminum chloride with potassium. The element now ranks among the most important of the metals, due largely to the achievements of Hall and Hérault (1886) in cheapening the process of extraction by electrolysis. (In 1856 the price was $76 per pound; in 1937 only 23 cents per pound.)

Aluminum finds extensive use in the industries. It is used in large quantities in the iron industry as a deoxidant. It is used in structural work of various kinds, automobile parts, airship frames and structures where lightness with strength is desired. It is used in making cooking utensils, aluminum foil for wrapping, aluminum paint. The metal is used in a number of alloys—golden bronze (Al, Cu), magnalium (Al, Mg), duralumin (Al, Cu, Mn, Mg), silicon aluminum alloy (Al, Si, Na), etc. Salts of aluminum are used as mordants, for water purification, paper industry, and various other purposes.

[2] Martin Tostered and Junius D. Edward, "The Discovery of Aluminum," Trans. Am. Electrochem. Soc., Vol. 51, 125 (1927).

filtering. The members of the hydrogen sulfide group are removed as usual with H_2S, the filtrate boiled to expel the excess of H_2S, iron oxidized with nitric acid, and aluminum, iron and chromium precipitated as hydroxides by addition of ammonium hydroxide in presence of ammonium chloride. On treating the precipitate with sodium peroxide, aluminum and chromium hydroxides dissolve, whereas ferric hydroxide remains insoluble. Aluminum hydroxide is precipitated by acidifying the alkaline solution with hydrochloric or nitric acid, and neutralizing with ammonia; chromium remains in solution.

Cobalt Nitrate Test.—The white gelatinous precipitate, obtained above, in the general procedure, is dissolved in a few drops of HNO_3, pure asbestos fibre, one half the size of a pea, is looped in a platinum wire, dipped into a solution of 0.05 N. cobalt nitrate, ignited and then dipped into the nitric acid solution containing the dissolved precipitate. The asbestos is again ignited. If aluminum is present a blue colored residue is obtained. The test is sensitive to 0.02 mg. aluminum.*

Aluminon Test.[3]—The dye aurin tricarboxylic acid forms a red lake with aluminum hydroxide. Iron and beryllium interfere and should be absent. The precipitate obtained with ammonia in the general procedure is dissolved in about 5 ml. of N HCl, 5 ml. of 3 N $NH_4C_2H_3O_2$ added, followed by 5 ml. aluminon reagent.[4] A mixture of NH_4OH and $(NH_4)_2CO_3$ [5] is now added until the solution is alkaline. A red precipitate is obtained if aluminum exceeds 0.1 mg. per 50 ml. Smaller amounts give a color varying from pink to deep red, depending on the amount of aluminum present. The method has been made quantitative, for determining minute amounts of aluminum.[6]

Alizarin S Test.—The reagent used is a 0.1% filtered solution of commercial alizarin S, the sodium salt of alizarin monosulphonic acid (yellow with acids, purple with alkalies). (Atack's method.)

To 5 ml. of the neutral or acid solution under examination is added 1 ml. of the reagent, and then ammonia until the solution is alkaline, as shown by the purple color. The solution is boiled for a few moments, allowed to cool, and then acidified with dilute acetic acid, when red coloration or precipitate remaining is conclusive evidence of the presence of aluminum. The red calcium, strontium, barium, zinc and magnesium salts, and salts of other metals later than Group II are readily soluble in cold dilute acetic acid, and do not interfere with the coloration. Interference of iron is prevented by addition of citric acid.

1, 2, 5, 8 Hydroxy Anthraquinone Test.—The test is carried out as follows: To 10 ml. of the neutral test solution add .25–1 ml. buffer solution (pH 5.4–5.8) and .3 ml. of .1% alcoholic 1, 2, 5, 8 hydroxy anthraquinone. A violet lake is produced if aluminum is present. The color of the lake varies from violet in concentrations of 1 mg. per liter to a faint violet for concentrations of .02 mg. aluminum per liter. This reaction is not influenced by the presence of alkali metals, alkaline earths, nor zinc, magnesium, cobalt, nickel, cadmium, lead, nor chromium salts. Copper and iron are objectionable due to the color of their

* See also recommendation by Carl Otto, J. Am. Chem. Soc., **48**, 1604 (1926).

[3] L. P. Hammett and C. T. Sottery, J. Am. Chem. Soc., **47**, 142, 1925.

[4] 0.2% soln.

[5] 10% soln. $(NH_4)_2CO_3$ in dil. NH_4OH (1 : 2).

[6] J. Am. Chem. Soc. **48**, 2125–26, 1926. A. R. Middleton.

salts. Tin, antimony, and bismuth produce precipitates at this pH. These precipitates are objectionable and may be removed by the addition of tartaric acid. (From Chem. Weekblad, **24**, 447–8 (1927); Chemical Abstracts, **22**, 40 (1928)).

Hydroxy methyl anthraquinone may be used in place of the 1, 2, 5, 8 hydroxyanthraquinone in the above procedure. (From Journal Am. Pharm. Assoc., **17**, 360–1 (1928)).

Lakes formed by aluminon with the hydroxides and the basic acetates of Be, Yt, La, Ce, Nd, Er, Zr and Th are all a deeper red than the lake produced by aluminum. All of the above are decolorized by moderate amounts of $(NH_4)_2CO_3$, except beryllium.

Microchemical detection—F. Rathgen. Z. anal. Chem., **53**, 33–7 (1913).

ESTIMATION

The determination of aluminum in ores is accomplished, generally, by gravimetric procedure. The volumetric determination is used in control processes of manufacture of aluminum compounds. The gravimetric determination of aluminum by precipitation of its hydroxide by hydrolysis, either by means of ammonium hydroxide, or by means of a salt of a weak acid, gives accurate results for pure salts of the element, but in the analysis of ores and minerals of aluminum or rocks and products containing other substances, serious error may result from the co-precipitation of other elements and acid radicals. For example silicon, chromium (if present in lower valences), beryllium, iron, titanium, zirconium and a number of the less common elements are also precipitated by NH_4OH. The presence of the phosphate radical will cause the precipitation of phosphates that are insoluble in alkaline solution including the alkaline earths, calcium, barium and strontium. The same can be said of arsenates, carbonates or fluorides. The removal of these interferences is necessary for correct results for aluminum. The gravimetric phosphate method for aluminum should also be followed with the same precautions for removal of interfering substances that precipitate under the conditions employed for aluminum.[7]

[7] L. A. Condon and J. A. Carter, "Critical Studies on Methods of Analysis. IV. Aluminum," Chem. News, **128**, 98, 100 (1924), place the following order of accuracy: (1) Craig's volumetric, (2) Schum's gravimetric, (3) Gatenby's volumetric, (4) Belasio's gravimetric, (5) Krug's gravimetric, (6) Ivanov's gravimetric and (7) Blum's gravimetric methods.

It must also be remembered that the hydroxide of aluminum is soluble in an appreciable excess of NH_4OH (pH 10), so that this reagent must be added cautiously, otherwise some aluminum will pass into the alkaline earth group causing an error in the determination of these elements.

The preparation of the material is governed by its nature. Substances high in oxides are usually attacked by acids, the insoluble residues being decomposed by subsequent fusion methods. Silicates are best decomposed by fusion with alkaline fluxes, sodium carbonate being commonly employed. Details of the procedures follow.

PREPARATION AND SOLUTION OF THE SAMPLE

In dissolving substances containing aluminum it will be recalled that alumina, although ordinarily soluble in acids, is very difficult to dissolve when it is highly heated. It may be best dissolved, in this case, by fusion with sodium carbonate or with acid potassium sulfate, followed by an acid extraction. The metal is scarcely acted upon by nitric acid, but is readily soluble in the halogen acids and in hot concentrated sulfuric acid.

General Procedure for Ores.—One gram of the finely powdered ore, taken from a representative sample, is placed in a platinum dish, 5 ml. of concentrated sulfuric acid are added, followed by about 20 ml. of concentrated hydrofluoric acid. The mixture is evaporated over a steam bath as far as possible and then taken to SO_3 fumes on the hot plate (*Hood*). Upon cooling, a little dilute hydrochloric acid is added and the mixture warmed. The solution is diluted with distilled water and filtered if any residue remains.

The insoluble residue remaining on the filter may be brought into solution by fusing the ignited residue with sodium carbonate or acid potassium sulfate. If barium is present sodium carbonate fusion is made and the melt extracted with water to remove the sodium sulfate. The residual carbonates may now be dissolved with hydrochloric acid.

Sulfide Ores should be oxidized with nitric acid and bromine according to the general procedure for decomposing pyrites in the determination of sulfur.

The solution of the sample having been effected, aluminum is separated from elements that interfere in its estimation. Directions for the removal of these substances are given under "Separations." The element is now in solution in such form that it may be determined gravimetrically or volumetrically.

Fusion Method. Sodium Carbonate.—The air-dried material, ground to a fine powder, is placed in a glass-stoppered bottle. If the determination is to be made on the dry basis, moisture is driven out by placing the material in the hot air or steam oven for an hour (100 to 110° C.). One gram sample, placed in a large platinum crucible, is mixed with 4 to 5 grams of anhydrous sodium carbonate and the material heated to fusion, the heating being continued until the molten mass appears clear. The liquid mass may be poured on a large platinum crucible lid, or if preferred, allowed to cool in the crucible, a platinum rod being held in the fusion until it solidifies. By gently heating the crucible over a flame the fusion loosens from the sides and may be lifted out on the rod. In either case the cooled mass is dissolved by placing it, together with the crucible in which the fusion was made in a casserole, and treating with

hydrochloric acid, the casserole being covered with a clock glass during the reaction.

Silica is removed by evaporating the solution to dryness on the water or steam bath and drying in the oven at 110° C. for an hour or more. The residue is extracted with hot dilute hydrochloric acid and silica filtered off.

If the solution is cloudy upon treatment of the fusion with acid, it indicates either the presence of barium sulfate or incomplete decomposition of the sample. In the latter case the residue is gritty and the fusion of this material should be repeated.

NOTE 1.—A sodium carbonate borax fusion mixture is recommended for decomposition of calcined bauxite and refractory high aluminous materials.[8, 9] See analysis of calcined bauxite.

NOTE 2.—An ammonium fluoride fusion is recommended for decomposition of refractory high aluminous materials in making the determination of sodium oxide.[10] See analysis of calcined ore.

Solution of Metallic Aluminum and its Alloys.—Aluminum is amphoteric in character, having the property of dissolving readily, not only in certain acids but also in alkaline solutions. Hydrochloric or perchloric acid, concentrated or moderately dilute, dissolves aluminum readily. The same is true of hydrofluoric and other binary halogen acids. Strong sulfuric acid—about 2 : 1—initially attacks aluminum readily, but the reaction quickly becomes sluggish. Dilute sulfuric acid has little action, but the addition of a small amount of a salt of mercury is very effective in promoting attack. This reaction is occasionally useful in analysis. The mercury salt is reduced to metallic mercury, amalgamates the aluminum, and thus the acid is brought in contact with the metal in a very reactive condition. Concentrated nitric acid has slow action on the commercial metal, and more rapid action on the alloys, but the addition of a small amount of a mercury salt, as in the case of sulfuric acid, causes solution to take place readily. The action of most other inorganic acids is slight unless mercury salts are added. Organic acids are, in general, not used as solvents of aluminum for analytical purposes because of their slow action. It is usual, in dissolving the metal in acid, to make use of mixtures of acids, such as the hydrochloric-nitric-sulfuric acid mixture which has been a standard reagent in the industry almost since its inception.

Bromine reacts with aluminum, but the reaction is difficult to control in aqueous solutions. The reaction with iodine is more readily controlled. Aluminum chloride is readily formed by the action of dry chlorine, or dry hydrogen chloride, upon the metal, and sublimes at a fairly low temperature. A method of attack based upon this reaction is used for the determination of certain non-metallic constituents.

Solutions of the fixed alkali hydroxides dissolve aluminum readily, the carbonates slowly, the bicarbonates, for analytical purposes, not at all. Ammonium hydroxide has only superficial action. Aluminum is attacked by salt solutions. Such reactions are seldom used for analytical purposes, although mercuric chloride solution has been applied as a solvent in some cases. Few

[8] Lundell, G. E. F., and Hoffman, J. I., Bureau of Standards, Jour. of Research, 1, 91–104 (1928).

[9] Lamar, M. O., Norton Company, private communication.

[10] Churchill, H. V., Bridges, R. W., and Miller, A. L., Ind. Eng. Chem., Anal. Ed. 8, 348 (1936).

other methods of attack are used—the foregoing are adequate to take care of almost any possible combination which might arise.

NOTES. **Analysis of Clay.**—In the complete analysis of clay, where the estimation of silica, aluminum, titanium, iron, calcium, magnesium, and the alkalies are required; it is advisable to use separate portions on individual or group determinations as follows: Fusion method for silica and titanium; acid attack with HF and H_2SO_4 for the determination of iron; determination of aluminum in the filtrate from silica, the iron and titanium being accounted for in the ammonia precipitate. Titanium may be determined in a separate sample by decomposing the clay by alkali carbonate fusion, and after the removal of silica, determining the titanium colorimetrically. Calcium and magnesium are determined in the filtrate from the aluminum determination. The alkalies may be best determined in a separate sample portion, first decomposing the material by the J. Lawrence Smith fusion method, as described in the chapter on the alkalies.

SEPARATIONS

General Considerations.—In the usual course of analysis, aluminum is in solution as a sulfate or as a chloride, silica having been removed by dehydration, as described under "Preparation and Solution of the Sample." The following interfering elements may be present in the solution: iron, manganese, arsenic, antimony, titanium, phosphoric acid, cerium and the other rare earths, and beryllium, tantalum, vanadium, chromium, zirconium, the alkaline earths, etc. (See precautions under Estimation.) In alloys of aluminum other elements may be added to this list. The separation more commonly required is from iron and titanium, which are commonly present with aluminum. In usual practice these are weighed together after ignition, then determined, either on a separate portion of the sample, or by solution of the precipitate by fusion with sodium carbonate or potassium bisulfate and subsequent extraction with hydrochloric acid.

Removal of Silica.—This compound has already been considered under "Preparation and Solution of the Sample," SiO_2 being removed by taking the solution to dryness, dehydrating the oxide by additional heating in the oven, followed by extraction of the soluble constituents with dilute hydrochloric acid and filtration. Under the first procedure for solution of the ore by sulfuric and hydrofluoric acids silica is expelled as gaseous SiF_4.

Separation from Iron, Zinc, Copper, Mercury, Bismuth, Titanium, Rare Earths, Beryllium, etc.—Aluminum chloride is precipitated from a concentrated solution of hydrochloric acid and ether saturated with HCl gas. Details of the procedure are given under the gravimetric methods for aluminum.

NOTE.—The following additional procedures for separation of iron and aluminum have been suggested:

(*a*) Precipitation of iron as FeS in presence of organic acids, citric, tartaric, salicylic, etc., aluminum remaining in solution.

(*b*) Precipitating iron by adding sodium peroxide to a cold neutral solution of the elements until the precipitate first formed dissolves, then decomposing the sodium ferrate by boiling, $Fe(OH)_3$ precipitates, Al remaining in solution. (Glaser, J. Soc. Chem. Ind., 1897, 936.)

(*c*) The neutral solution of the elements is boiled with freshly precipitated MnO_2, which causes the precipitation of iron as $Fe(OH)_3$, while aluminum remains in solution. (Chromium also passes into the filtrate.)

(*d*) Precipitation of iron from acid solutions by means of amino-nitrosophenylhydroxylamine, (cupferron), aluminum remaining in solution. (O. Baudisch, Chem.

Ztg., 33, 1298, 1905. *Ibid.*, 35, 913, 1911; O. Baudisch and V. L. King, J. Ind. Eng. Chem., 627, 1911.)

(*e*) Precipitation of aluminum (together with phosphoric acid, if present), by phenylhydrazine, added to the reduced, weakly acid or neutral solutions. Iron, cobalt, nickel, calcium, and magnesium remain in solution. (Hess and Campbell, Chem. News, 81, 158. Engles, J. Soc. Chem. Ind., 1898, 796.)

(*f*) Electrolytic separation of iron by amalgamation with mercury cathode and determining aluminum in the solution. (Kretzschmar, J. Soc. Chem. Ind., 1890, 1064; Kolin and Woodgate, J. Soc. Chem. Ind., 1889, 260.)

Phosphoric Acid.—In presence of phosphoric acid, the phosphates of iron and alumina together with the phosphates of the other elements of the group and those of the alkaline earths will be precipitated upon making the solution alkaline with ammonia. Should iron and alumina be the only elements of these two groups present in the solution, they may be precipitated together as phosphates, iron determined by titration and calculated to the phosphate salt, and alumina obtained by difference. Occasionally, however, it is necessary to remove phosphoric acid.

Removal of Phosphoric Acid.—The material is fused with about six times its weight of a mixture of 4 parts Na_2CO_3 and 1 part SiO_2 (silex), and the melt extracted with water containing ammonium carbonate. Iron and aluminum remain on the filter, upon filtration, while sodium phosphate passes into solution. Both the precipitate and filtrate contain silica. The precipitate of iron and alumina is dissolved in hydrochloric acid and taken to dryness, the residue dehydrated as usual, then treated with dilute hydrochloric acid and silica filtered off. The solution contains iron and aluminum in form of chlorides.

Separation of Aluminum from Chromium.—The solution is made strongly alkaline with sodium or potassium hydroxides and chromium oxidized by passing in chlorine gas or by adding bromine. The solution is now acidified with nitric acid and aluminum hydroxide precipitated by addition of ammonium hydroxide, chromium remaining in solution as a chromate.

Separation of Aluminum from Zinc.—Aluminum and zinc can be separated quantitatively by precipitating the aluminum as lithium aluminate from solutions containing ammonium acetate; the zinc remains in solution and may be determined in the filtrate. (Fish, F. H. and Smith, J. M., Ind. Eng. Chem., Anal. Ed., 8, 349 (1936).)

Separation of Aluminum from Manganese, Cobalt, Nickel, Zinc, the Alkaline Earths, and Alkalies.—Iron and aluminum are precipitated as basic acetates, the other elements passing into solution. Details of the procedure are given under the basic acetate method (see Manganese chapter). If aluminum is preponderant there is danger of incomplete precipitation by this method.

In absence of phosphates, these elements do not interfere in the determination of aluminum by precipitation as the hydroxide.

Separation of Aluminum from Titanium.—Details of the procedure are given under "Titanium."

Separation of Aluminum from Uranium.—Aluminum is precipitated as $Al(OH)_3$ in presence of a large amount of ammonium salts by addition of a large excess of ammonium carbonate and ammonium sulfide, while uranium remains in solution as the complex compound $UO_3(CO_3)_3(NH_4)_4$.

Separation from Beryllium.—Aluminum is soluble in the fixed alkalies and remains in solution on boiling; beryllium also dissolves, but is precipitated on

boiling. *Beryllium is soluble in an excess of ammonium carbonate, aluminum is not. Beryllium is separated from aluminum by precipitation of $AlCl_3$ with HCl gas.* Also by precipitation of aluminum oxyquinolate with 8-hydroxyquinoline. See Determination of Beryllium in Aluminum, H. V. Churchill, R. W. Bridges, and M. F. Lee, Ind. Eng. Chem., Anal. Ed. **2**, 4, 404–5 (1930).

Separation from Zirconium, Rare Earths, and from Manganese, Iron and Titanium.—(Absence of magnesium and nickel which carry down aluminum.) The solution is nearly neutralized by NaOH and then poured into a large excess of NaOH solution. $Al(OH)_3$ dissolves, while the elements stated separate as precipitates. Titanium, if greatly preponderant, will not precipitate completely. Phosphorus, tungsten, molybdenum, vanadium, if present, accompany aluminum and must be subsequently separated. If the precipitate is large a double precipitation is advisable.

Separation of Aluminum from Iron, Titanium, Zirconium, Vanadium, Tantalum, Columbium, Tin, Quadrivalent Uranium.—Addition of a 6 per cent solution cupferron added to an ice cold acid solution precipitates these elements while aluminum passes into solution together with chromium, manganese, hexavalent uranium, nickel, zinc. The reagent in the filtrate is destroyed by evaporation with HNO_3 and H_2SO_4 before proceeding with the determination of the aluminum, etc.

Separation of Aluminum from Phosphates, Arsenates, Fluorides, Borates, Molybdenum, Columbium, Tantalum, Titanium, Vanadium, Beryllium, Uranium by Precipitation of Aluminum with 8 Hydroxyquinoline.—See original articles—G. E. F. Lundell and H. B. Knowles, Bureau of Standards, J. of Research, **3**, 91 (1929), and I. M. Kolthoff and E. B. Sandell, J. Am. Chem. Soc., **50**, 1900 (1928). Addition of H_2O_2 is required for removal of Cb, Mo, Va, Ta and Ti in ammoniacal solution; $(NH_4)_2CO_3$ for solution of U; and acetic acid for removal of Be. See page 12.

Separation from Nickel.—Nickel is precipitated by electrolysis with a mercury cathode, aluminum remaining in solution.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF ALUMINUM

DETERMINATION BY HYDROLYSIS OF AN ALUMINUM SALT WITH AMMONIUM HYDROXIDE

Principle.—The method depends upon the hydrolysis of a soluble salt of aluminum by neutralizing the free and combined acid with ammonia. This hydrolysis takes place in presence of ammonium chloride, which prevents the precipitation of magnesium hydroxide by NH_4OH, the common ion, NH_4^+,

repressing the ionization of the base, NH_4OH. (See Notes.) The direct determination of aluminum by this procedure excludes the presence of elements undergoing hydrolysis with similar conditions. If present the following elements will precipitate with aluminum Fe^{+++}, Cr^{+++}, Cb, Be, In, Ga, Ce, Zr, and other rare earths, Ta, Ti, Tl, Si, V. Boron if present will accompany aluminum. The arsenate or phosphate or carbonate radical must be absent. See under Estimation.

The precipitation of aluminum hydroxide is complete between pH 7–7.5. Indicators showing an alkaline reaction at 7–7.5 should be used. With a pH exceeding 10 the hydroxide is appreciably soluble, aluminum later appearing with the calcium and magnesium precipitates.

The method is applicable to the determination of aluminum in its commercial ores, where but slight interference with other elements is met, iron and titanium being the chief offenders.[11]

Reaction.—$AlCl_3 + 3NH_4OH \rightarrow Al(OH)_3 + 3NH_4Cl$.

Procedure.—To the solution, free from phosphoric or arsenic acid and elements that would precipitate with aluminum (see list above) add 5 g. NH_4Cl and 5 ml. of concentrated HNO_3 and heat the solution to boiling, then allow to cool. Add 2–3 drops of an indicator with a pH range between 6.5–7.5 and then very carefully from a burette, dropwise, NH_4OH until the alkaline color is obtained. (pH 7.5.) The NH_4OH should be free from carbonate. Heat the solution to boiling and filter. Wash the precipitate with a 2 per cent solution of NH_4NO_3.

Dissolve the precipitate in a small amount of hot, dilute HCl and reprecipitate to eliminate, as completely as possible, occluded substances. Be sure that the solution of the hydroxide by HCl is complete, and that the alkalinity in re-precipitation does not exceed the limit recommended.

Wash the precipitate free of chlorides using the 2 per cent NH_4NO_3 solution. Drain, then place filter and its contents in a platinum or porcelain crucible. Ignite gently at first until the paper is thoroughly charred; gradually increasing the heat. Cover the crucible and heat to a glowing white temperature. Cool in a desiccator, then weigh rapidly. Repeat the heating, cooling and weighing until a constant weight is obtained. The residue is Al_2O_3.

$$Al_2O_3 \times 0.5291 = Al.$$

Results are usually reported as Al_2O_3.

NOTES.—Error in the aluminum determination may arise from the co-precipitation of other substances, that require an excess of NH_4OH for their re-solution, i.e., Cu, Ni, Co, Zn. If the carbonate radical is present in the ammonia, a number of substances will precipitate on the addition of this reagent. Upon long standing with frequent exposure to air the ammonia takes up CO_2, forming carbonate of ammonia. Freshly distilled ammonia, the carbonate being precipitated by addition of lime in the distilling flask, is best kept in a ceresine or paraffine bottle. It will then remain free from silica, which it invariably contains when confined in glass bottles.

Long heating of the mixture containing the aluminum precipitate is objectionable.

[11] If iron and titanium are present, these may be determined colorimetrically on separate portions and their weights, as oxides, deducted from the residue of the ammonia precipitate, the difference being due to alumina.

1. The solution is apt to become acid owing to the decomposition of ammonium salts and the volatilization of ammonia.

2. The precipitate will become slimy and will be difficult to wash and filter. It is preferable to redissolve and again precipitate if this condition occurs.

3. The CO_2 of the air is apt to be absorbed by the solution, causing the precipitation of calcium carbonate, etc., should the solution be exposed for any length of time.

4. Silica from the beaker will contaminate the precipitate.

Hence it is advisable to filter as soon as possible after making the precipitation of $Al(OH)_3$.

Washing the precipitate with ammonium nitrate prevents the aluminum from passing through the filter and keeps it from packing. It favors the formation of the insoluble hydrogel form of the hydrate while preventing the formation of the soluble hydrosol. Ammonium chloride may be used in place of nitrate.

Aluminum hydroxide is soluble in acids and alkalies. The ignited oxide, Al_2O_3, is insoluble in acetic acid but is soluble in mineral acids and the fixed alkalies. It is rendered very difficultly soluble in acids by strong ignition, generally requiring fusion with sodium carbonate or potassium bisulfate with subsequent acid treatment to effect solution.

A yellow or reddish precipitate indicates the presence of iron, an element frequently present with aluminum. Should this be the case, iron must be determined, either in a separate portion of the sample, or in the residue obtained by the procedure outlined. The amount of Fe_2O_3 is subtracted from the total residue, and Al_2O_3 obtained by difference.

If ***phosphoric acid*** is present the phosphate of alumina will precipitate together with the phosphates of elements insoluble in alkaline solutions. Should phosphoric acid be present either its removal is essential, or the phosphate method for alumina should be followed.

Alkali salts may be occluded by the aluminum precipitate.

Fluorides hinder the precipitation of aluminum. Evaporation to dryness with sulfuric acid and heating the residue to redness will transform fluorides to oxides and overcome this difficulty.

Sulfates tend to hold up aluminum from precipitation and a certain amount of sulfuric acid is occluded by the aluminum hydroxide precipitate. Magnesium is more apt to precipitate with alumina in presence of sulfates. Ammonium chloride greatly lessens this difficulty.

Traces of alumina may be recovered from the filtrate by evaporation to dryness, ignition and resolution with HCl. The $Al(OH)_3$ is now precipitated with NH_4OH.

Since alumina absorbs moisture from the air, the crucible containing this compound should be kept covered in a desiccator until weighed.

Ammonium hydroxide, in presence of sufficient NH_4Cl, will not precipitate $Mg(OH)_2$, since the addition of NH_4Cl increases the ammonium ions in the solution and, by the common ion effect, represses the hydroxyl ions of the base, NH_4OH, so that there are insufficient hydroxyl ions for the solubility product of $Mg(OH)_2$ to be exceeded; therefore magnesium remains in solution.

DETERMINATION OF ALUMINUM BY HYDROLYSIS, NEUTRALIZING THE MINERAL ACID BY ADDITION OF A SALT OF A WEAK ACID. SODIUM THIOSULFATE METHOD

If a salt of a weak acid and strong base is added to a neutral or slightly acid solution of an aluminum salt containing a mineral acid, transposition takes place and aluminum is hydrolyzed.

Reaction.—$2AlCl_3+3Na_2S_2O_3+3H_2O=2Al(OH)_3+6NaCl+3SO_2+3S.$

Procedure.—If the solution is acid, dilute ammonia is added until a precipitate forms that dissolves with difficulty, but not enough ammonium hydroxide to cause a permanent precipitation. The solution is diluted so that it contains about 0.1 g. Al per 200 ml., then an excess of sodium thiosulfate is

added, and the solution is boiled free of SO_2. Al $(OH)_3$ precipitates along with free sulfur. If iron is absent it is advisable to add a few drops of ammonium hydroxide until the solution has a slight odor of ammonia. The mixture again boiled is filtered and the residue of $Al(OH)_3$ and sulfur washed with hot water containing about 2 g. NH_4NO_3 per 100 ml. The precipitate is dried, separated from the filter, the latter ignited and the ash added to the main precipitate. Alumina is now determined by blasting to constant weight, the residue being weighed as Al_2O_3.

NOTES.—The above method may be employed for separation of aluminum from iron, the addition of ammonia, following the neutralization of the mineral acid by thiosulfate being omitted. The precipitation of $Al(OH)_3$ by this procedure gives a more dense and better filtering precipitate than does ammonia alone.

NOTE.—G. Wynkoop suggests the use of sodium nitrite as the salt of a weak acid for neutralizing the mineral acid. (J. Am. Chem. Soc., **19**, 434 (1897).)

I. Ivanov recommends neutralizing the aluminum solution with sodium thiosulfate then diluting to 100 ml. and adding potassium iodide, followed by a 3% solution of KIO_3 and additional KI (10% soln.) until precipitation is complete. The excess of iodine is expelled by boiling. The $Al(OH)_3$ is filtered and washed with NH_4NO_3 soln. (2% soln.) and then ignited to Al_2O_3.

Lewis B. Skinner suggests the following procedure: To about 150 ml. of acid solution containing aluminum, but free from phosphoric acid and elements precipitable by ammonium hydroxide, are added 5 grams of ammonium chloride and carbonate-free ammonium hydroxide, the latter drop by drop from a 50-ml. burette until a small piece of litmus paper just turns from red to blue. One ml. excess is now added, the solution is just brought to a boil, the precipitate is allowed to settle a few minutes off the hot plate so as to avoid loss of ammonia, the solution is decanted through a filter paper and followed by the precipitate, the precipitate is loosened from the paper by the first wash-water jet to provide for relatively rapid filtration and the beaker is cleaned and further washings are done.

H. H. Willard and N. G. Tang recommend the determination of aluminum by precipitation of urea. (Ind. Eng. Chem., Anal. Ed., **9**, 357 (1937).) Aluminum can be accurately separated from large amounts of calcium, barium, magnesium, manganese, cobalt, nickel, zinc, iron, cadmium, and copper by precipitation as the dense basic succinate by boiling with urea the acid solution containing succinic acid. Hydrolysis of the urea forms ammonia gradually in an homogeneous solution, resulting in a pH of 4.2 to 4.6. Owing to the dense nature of the precipitate, it is easily filtered and washed and shows much less adsorption of other salts than does the precipitate obtained by the usual methods. The basic sulfate precipitated in this way is also dense, but the pH must be 6.5 to 7.5 and separations in certain cases are less satisfactory. The accuracy of separations made by the urea method is far superior to that obtainable by the use of ammonia. This is attributed to a combination of four important factors —a dense precipitate, a slow, uniform increase in pH, a homogeneous solution, and a low final pH.

THE 8-HYDROXY QUINOLINE (OXINE) METHOD FOR DETERMINING ALUMINUM[12]

The compound 8-Hydroxy Quinoline (Oxine), $H.C_9H_6NO$, forms compounds with metals, in which the metal replaces the hydrogen as shown by the aluminum and magnesium compounds: $Al(C_9H_6NO)_3$ and $Mg(C_9H_6NO)_2$. The following elements precipitate with "oxine";—Ag, Al, Cb, Co, Hg, Fe, Mn, Ni, Pb, Sb, Ta, Ti, U, V, Zn and Zr from acetate-acetic acid solution; and with the exception of Ag, the above elements and in addition Ba, Be, Ca, Mg, Sn, Sr precipitate from alkaline solutions. The quantitative precipitation of the oxine of aluminum from a weak acid solution and of magnesium from an alkaline solution have been successfully utilized in their determination. Kolthoff recommends the following method.[13]

Procedure.—The solution of aluminum, containing not over 0.1 g. Al_2O_3 per 100 ml., and free from interfering elements, is treated with 2–5 ml. of 4 N acetic acid and heated to near boiling (about 90° C.), and 2–10 ml. of 2 N sodium or ammonium acetate added. The precipitate, $Al(C_9H_6NO)_3$, is filtered off and washed. Aluminum is now estimated by either drying the precipitate to constant weight at 130° C. (the precipitate contains 11.1% Al_2O_3) or by titration.

Titration.—The precipitate is transferred to the vessel in which the precipitation was made, using precautions to recover all of the compound. 15–20 ml. of 4 N HCl are added and the mixture heated until all of the oxine has dissolved. After cooling, 1–2 drops of methyl red indicator are added, and about 0.5 g. KBr. The solution is titrated to a yellow color with standard bromate solution. 1 ml. 0.1 N $KBrO_3$ corresponds to 0.000225 g. Al.

NOTES.—The alcoholic solution of oxine (5% oxine) may be replaced by a water solution, the reagent being prepared by adding to a few ml. of phenylhydrazine cold saturated solution of SO_2 until the precipitate that first forms dissolves and then phenylhydrazine, drop by drop, with vigorous stirring, until free from SO_2 odor. The aluminum oxine can best be precipitated from an acetic acid solution of oxine (5 per cent in 4N acetic acid solution) than from an alcoholic solution, as alcohol has a solvent action on the precipitate, causing results 1 per cent too low.

PRECIPITATION OF ALUMINUM AS ALUMINUM CHLORIDE[14]

Principle.—Gooch and Havens found that aluminum chloride is practically insoluble in a mixture of concentrated hydrochloric acid and ether saturated with HCl gas, 5 parts of $AlCl_3.6H_2O$ equivalent to 1 part of Al_2O_3 dissolving in 125,000 parts of the mixture. The method serves for a separation of aluminum from iron, beryllium, zinc, copper, mercury and bismuth, the chlorides of these elements being soluble under the above conditions. Barium, however, is precipitated as a chloride with aluminum, if it is present in the solution.

Procedure.—To the concentrated aqueous solution of aluminum is added a convenient volume of strong hydrochloric acid (15 to 25 ml.) and an equal

[12] R. Berg, J. prakt. Chem., **115**, 178 (1927); I. M. Kolthoff, Chem. Weekbl., **24**, 606 (1927); F. L. Hahn, Chem. Ztg., **50**, 754 (1926); ibid., Z. Anal. Chem., **71**, 122 (1927).

[13] Volumetric Analysis, II, Kolthoff and Furman, p. 484. J. Wiley and Sons, New York (1929).

[14] F. A. Gooch and F. S. Havens, Am. Jour. Sci. (4), **2**, 416. F. A. Gooch, "Methods in Chemical Analysis."

volume of ether. The mixture is best placed in a large platinum crucible, which is kept cool in running water. HCl gas is passed into the solution to saturation. The precipitated chloride of aluminum is filtered upon asbestos in a weighed Gooch crucible and then washed with a mixture of ether and water 1 : 1, saturated with HCl gas. The precipitate is dried for half an hour at 150° C., then covered with a layer of C.P. mercuric oxide (1 gram) and heated at first gently over a low flame (hood) and then blasted to constant weight. The residue is weighed as Al_2O_3.

NOTES.—HCl gas may be conveniently generated, with an apparatus as shown in Fig. 1. Concentrated hydrochloric acid is added to concentrated sulfuric acid below its surface by means of a capillary tube.

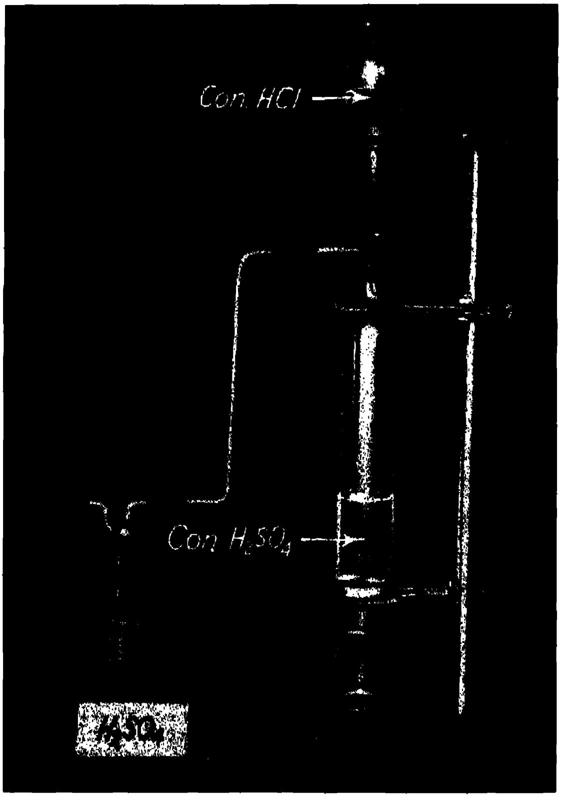


FIG. 1.—Hydrogen Chloride Gas Generator. HCl is discharged under surface of H_2SO_4 by means of a capillary tube.

The filtrate from aluminum contains iron, beryllium, copper, zinc, etc., if these are present in the original solution. If much iron is present it is necessary to increase the amount of ether to prevent precipitation of the ferric salt.

DETERMINATION OF ALUMINUM AS PHOSPHATE

The method is accurate for the determination of small amounts (under 100 mg.) provided other elements precipitated as phosphates are absent. The commonly interfering elements are Fe^{+++}, Mn, Zr, Zn, Ca. If present,

provision must be made for their removal. This is accomplished in part by neutralizing the solution with NaOH and pouring this solution into a dilute solution of NaOH so that there is an excess of 10% of NaOH, (Al free). The solution is diluted to definite volume, a portion filtered off and an aliquot portion taken for the aluminum determination. Nickel and manganese may still be in solution and provision must be made for their removal if present. Details of the following method are taken from the recommended procedure by G. E. F. Lundell and H. B. Knowles (J. Am. Chem. Soc., **44**, 1136 (1922)).

Procedure.—The solution free from interfering elements is neutralized with HCl, if alkaline, and 10 ml. excess of HCl added followed by dilution to 400 ml. A ten fold excess (generally 1g. is sufficient) of $(NH_4)_2HPO_4$ is added and macerated filter paper (1 sheet 11 cm. No. 40 Whatman). The solution is made alkaline to methyl orange indicator (2 drops) by addition of NH_4OH and then 0.5 ml. HCl is added. The solution is heated to boiling and 30 ml. of 25% solution of ammonium acetate are added and the solution boiled for about five minutes. The aluminum phosphate is filtered off and washed with a hot 5 per cent solution of NH_4NO_3 until free of chlorides ($AgNO_3$ test). The filter should not be allowed to run dry during the washing. The paper and residue are now dried and then ignited gently in an open crucible until the carbon of the filter is consumed and then at bright red heat (1000° C.) until a constant weight is obtained. The phosphate is hygroscopic so that the weighing must be done rapidly. Weigh as $AlPO_4$

$$AlPO_4 \times 0.2211 = Al; \quad AlPO_4 \times 0.4178 = Al_2O_3.$$

NOTES.—With larger amounts of aluminum it is practically impossible to remove the excess of P_2O_5 by washing.

VOLUMETRIC METHODS FOR THE DETERMINATION OF ALUMINUM

VOLUMETRIC DETERMINATION OF COMBINED ALUMINA IN ALUMINUM SULFATE AND ALUMINUM SALTS

Introduction.—Aluminum salts dissociate in hot solutions and react acid to phenolphthalein indicator; the acid readily combines with fixed alkalies, forming the neutral alkali salt. The end point of the reaction is indicated by the pink color produced upon phenolphthalein by the excess of alkali. From the amount of caustic required the percentage of combined Al_2O_3 may be calculated. The

following reaction takes place:

$$Al_2(SO_4)_3+6NaOH=2Al(OH)_3+3Na_2SO_4.$$

Procedure.—The factor weight,[15] 3.3980 grams, is dissolved in a 4-in. casserole with 100 ml. of distilled water, 1 ml. of phenolphthalein indicator added, and the sample titrated boiling hot [16] with N/2 NaOH, added from a chamber burette, graduated from 50 to 100 ml. in tenths of a ml.[15] The solution is kept boiling during the titration and is constantly stirred. Towards the end of the reaction the alkali is added cautiously drop by drop until a permanent pink color is obtained.

Ml. of NaOH required divided by 4 = per cent combined Al_2O_3.[17]

Combined Al_2O_3+free Al_2O_3 = total Al_2O_3.

NOTES.—If iron is present a correction must be made for it after determining the ferrous and ferric forms as given below.

The amount of phenolphthalein indicator used should be the same in each determination. An excess of indicator causes low results. It has been noted in case of alums where iron does not interfere that best results are obtained with three or four drops of phenolphthalein solution. Iron tends to mask the end point, hence a larger amount of indicator is necessary if this is present.

Correction for Iron if Present.—Since iron salts will also dissociate and titrate with aluminum salts, by this method a correction has to be made for iron if present. Total Al_2O_3 in presence of iron =

combined $Al_2O_3-(FeO\times.47+Fe_2O_3\times.64)$+basic Al_2O_3+an additive factor.

The additive factor is obtained by subtracting

(Combined Al_2O_3+basic Al_2O_3) $-(FeO\times.47+Fe_2O_3\times.64)$ volumetric,

from total Al_2O_3 obtained by gravimetric analysis of an average sample.

Ferrous Iron, Ferric Iron, and Total Iron.—A five-gram sample is dissolved in water and the iron oxidized with a few drops of strong potassium permanganate solution; the solution should be pink; the excess of permanganate is destroyed by a drop or so of normal oxalic acid solution and the total iron determined by stannous chloride solution method for iron. On a separate sample ferric iron is determined. Ten grams of the sample are dissolved in an Erlenmeyer flask by boiling with hydrochloric acid, 2 : 1, in an atmosphere of CO_2 to prevent oxidation, and the iron titrated with standard stannous chloride. The difference between total iron as Fe_2O_3 and ferric oxide = ferrous iron in terms of Fe_2O_3. This multiplied by 0.9 = FeO.

COMBINED SULFURIC ACID

Provided no free acid is present, the per cent combined sulfuric acid in aluminum sulfate is obtained by multiplying the ml. caustic titration for total alumina by 0.72.

[15] Large samples must be taken for salts containing less than 13 per cent Al_2O_3 if the chamber burette is to be used. E.g., potash alum twice this amount is advisable.

[16] Otto Schmatolla, Berichte, 38, No. 4. Chem. News, 91-2375-236 (1905).

[17] If free acid is present (see next method), the equivalent volume in terms of ½ N acid must be deducted from the total titration for combined alumina before dividing by 4.

In case free acid is present, the per cent free acid deducted from total acid found by titration gives combined acid.

Sulfuric acid combined with the fixed alkalies is not titrated.

DETERMINATION OF FREE ALUMINA OR FREE ACID BY THE POTASSIUM FLUORIDE METHOD

Introduction.—The method suggested by T. J. I. Craig (J. Soc. Chem. Ind., **30**, 185, 1911), has been modified by Scott,[18] after an investigation of the details involved. In this modified form it has been used successfully as a rapid works method. Frequent gravimetric checks on a large number of determinations have shown it to be accurate.

The procedure is based upon the fact that an excess of neutral potassium fluoride decomposes aluminum salts, forming two stable compounds, which react neutral to phenolphthalein, while the free acid remains unaltered, the following reaction taking place:

$$Al_2(SO_4)_3+12KF+xH_2SO_4=2AlF_33KF+3K_2SO_4+xH_2SO_4.$$

The precipitate AlF_33KF is insoluble in an excess of the potassium fluoride reagent and is not appreciably attacked by acids or alkalies. Although theoretically about 7 parts by weight of potassium fluoride is sufficient to combine with 1 part of aluminum sulfate, in practice it is advisable to use twice this amount.

Reagents Required.—*Half Normal* solutions of sulfuric acid and potassium hydroxide.

Phenolphthalein indicator, 0.1% alcoholic solution.

Potassium fluoride solution; made by dissolving 1000 grams of potassium fluoride in about 1200 ml. of hot, CO_2-free water, then neutralizing the solution with hydrofluoric acid or potassium hydroxide as the reagent may require, using 5 ml. of phenolphthalein as indicator. Dilute sulfuric acid may be used in place of hydrofluoric acid in the final acid adjustment to get a neutral product. One ml. of the solution in 10 ml. of CO_2-free water should appear a faint pink. The concentrated mix is filtered if necessary and then diluted to 2000 ml. with CO_2-free water. The gravity will now be approximately 1.32 or about 35° Bé. One ml. contains 0.5 g. potassium fluoride.

Method of Procedure

Solids.—3.398 g. of the finely ground sample, or an equivalent amount in solution (100 ml. of sample containing 33.980 g. per liter), are taken for analysis. The powder is dissolved by boiling with 100 ml. of distilled water in a 4-in. casserole with clock glass cover. To the hot solution 10 ml. of N/2 H_2SO_4 are added and after cooling to room temperature, 20° C., 18 to 20 ml. of the potassium fluoride reagent are added and 0.5 ml. of phenolphthalein. The solution is now titrated with N/2 KOH, added drop by drop until a delicate pink color, persisting for one minute, is obtained. This titration shows whether the product is basic or acid.

Basic Alumina.—This is indicated when the alkali back-titration is less than the amount of acid added. Free Al_2O_3 = (ml. H_2SO_4 − ml. KOH) ÷ 4.

[18] W. W. Scott, J. Ind. Eng. Chem., **7**, 1059, 1915.

Free Acid.—In case the back-titration of the alkali is greater than the ml. of acid added, free acid is present. Free acid = (ml. KOH − ml. H_2SO_4) × 0.72.

Liquors.—In works control it is necessary to test the concentrated liquors to ascertain whether these are basic or acidic. The Bé. or sp.gr. of the solution having been taken, 5 ml. is diluted to 100 ml. with distilled, CO_2-free water. If H_2S is present, it is expelled by boiling the solution, which should be acid, 10 ml. of N/2 H_2SO_4 is added, the solution cooled, and KF and phenolphthalein added and the titration made as in case of solids.

If basic (ml. H_2SO_4 − ml. KOH) × (.0245 × .3465 × 100) ÷ (5 × sp.gr.) = Al_2O_3.

If acid (ml. KOH − ml. H_2SO_4 × 2.45) ÷ wt. of sample = per cent free acid (H_2SO_4).

If neutral, the back titration of the alkali is the same as the ml. acid added.

Notes.—CO_2-free water must always be used when phenolphthalein indicator is necessary. This may be obtained by boiling distilled water for several minutes to expel CO_2. This reagent is very sensitive to carbonic acid.

If the sample does not dissolve clear, a prolonged digestion with previous addition of the required amount of standard acid, 10 ml., is advisable. This is best accomplished in an Erlenmeyer flask with a return condenser.

Darkening of the solution during the back titration with the alkali, indicates that an insufficient amount of fluoride has been added. If this is the case it will be necessary to make a fresh determination.

The fluoride method has the following advantages. Determinations may be made by gas or electric light. The end point is easily detected. No neutral standard is necessary as in case of the tint method.

Ammonium salts, if present, must be expelled by boiling the sample with an excess of standard KOH and this excess determined.

3.3980 = 2.452 × .3465 × 4 (i.e., gms. H_2SO_4 per 100 ml. N/2 acid multiplied by 4 times factor to equivalent Al_2O_3). Derived directly from mol. wt. of Al_2O_3 = 0.10194 × 100 × 4) ÷ (6 × 2). 0.7216 = 2.8862 ÷ 4 (i.e., factor Al_2O_3 to H_2SO_4 ÷ 4).

COMMERCIAL METHODS FOR EVALUATION OF ALUMINUM ORES AND ANALYSIS OF ALUMINUM

DETERMINATION OF THE AVAILABLE ALUMINA IN ALUMINOUS ORES[19]

Various methods are used for the determination of available alumina by consumers of aluminous ores. A method may be either an acid or caustic digestion, and is designed to give information indicating the amount of alumina which is recoverable by the operator's process. The following is an example of a method based on sulfuric acid digestion.

[19] By Harold E. Martin.

This method is based on the solution of the sample in a known amount of sulfuric acid, and the titration of the excess acid with standard sodium hydroxide solution, and the alumina estimated from the amount of acid used to combine with it. It has been proven with long practice that this method is accurate within 0.5%, and is very satisfactory as a works control method. It is much more rapid than the regular gravimetric procedure.

Take a five gram sample that has been ground to pass through a 60-mesh sieve and put it into a 300 ml. Kjedahl flask with about 28 to 30 grams of 40° Bé sulfuric acid, which is weighed from a weighing burette. (This acid may be measured with a burette and the weight calculated if so desired with a reasonable chance of error introduced.) Digest this at a gentle boil for one hour, giving the flask an occasional shaking. Care must be taken that good condensation is effected, otherwise a loss in acid will give high results. After the digestion wash down the condenser and filter the insoluble residue off on a Buechner funnel with suction, washing the residue acid free. Make the filtrate up to 2000 ml. in a volumetric flask. To a 200-ml. aliquot add 20 ml. KF reagent, and 1 ml. phenolphthalein indicator and titrate to a permanent pink with standard N/10 NaOH.

Reagents.—The 40° Bé acid must be made up very accurately and standardized against standard caustic.

1000 grams of potassium fluoride are dissolved in 1200 ml. of hot CO_2 free water, and then neutralized with HF or KOH as may be necessary, using phenolphthalein indicator. Filter this solution and dilute to 2000 ml. This solution should be kept in a wax-lined bottle.

Take 20 ml. of KF reagent and add 5 ml. of N/2 NaOH and one ml. of phenolphthalein indicator, and titrate with N/2 H_2SO_4. Apply this correction to the titration of the sample.

Calculations.—

$$\frac{(\text{ml. N/10 } H_2SO_4 - \text{ml. N/10 NaOH}) \times 0.3465 \times 100}{\text{weight of sample}} = \%Al_2O_3 + Fe_2O_3$$

% $Fe_2O_3 \times .64 = Fe_2O_3$ equivalent to Al_2O_3 which can be subtracted from the total oxides above, the result being the available alumina.

COMMERCIAL METHODS FOR THE ANALYSIS OF BAUXITE, CALCINED ORE (ALUMINA), AND ALUMINUM HYDRATE

In the analysis of aluminous materials it is only in the separation of elements that the procedures differ. After the proper separations have been made the actual determination of the elements is, in most cases, the same. To save repetition, the procedures for determining the elements will be grouped together and placed before the discussion of separations made under the analysis of bauxite, alumina, and aluminum hydrate. Methods for preparation of reagents and standard solutions are appended, pp. 29–32.

DETERMINATION OF ELEMENTS

1. **Preparation of Sample.**—A representative and homogeneous sample is essential before starting an analysis. Since ore sampling varies with each individual material, no general procedure will be given here. Precautions should be taken to avoid contamination from crusher or mortar. Grinding to excessive fineness should be avoided since water may be lost, or the composition of the sample altered. In case extreme fineness is desired for particular determinations, as, for example, the determination of total alkalies, a separate portion of the ground sample should be further reduced.

2. **Determination of Moisture.**—The analysis of ore materials is usually carried out on a dried sample and reported on a dry basis. When the moisture content is desired, it should be determined by drying a suitable amount of the original material, coarsely ground with a minimum of exposure, to constant weight at 140° C. For routine analysis, drying at 110° C. is permissible. For the determinations other than moisture, grind a sample to suitable fineness and dry before weighing out the analytical portions.

3. **Determination of Loss on Ignition.**—Place a suitable amount of dried sample in a weighed, covered crucible. Heat gently at first, then at a gradually increasing temperature. Finally ignite at 1100° C. for one-half hour, cool, and weigh. Reignite to constant weight. Diminution in weight represents loss on ignition.

4. **Determination of Silica.**—

Reagents.—1–1 sulfuric acid. Hydrofluoric acid, 48%.

Procedure.—Dehydrate the silica by evaporating until sulfur trioxide fumes have been given off for some time. Cool, add a little cold water, dilute, and boil to solution of salts. Filter and wash well with hot water. For accurate analysis, the dehydration and filtration should be repeated. Ignite the precipitate(s) to constant weight, cool, and weigh. Moisten the silica with a few drops of 1–1 sulfuric acid, and add hydrofluoric acid. Evaporate to dryness, ignite, cool, and weigh. For routine analysis one treatment with hydrofluoric acid is usually sufficient. Where greater accuracy is desired, repeat the volatilization. The sulfuric-hydrofluoric acid addition should be repeated until constant weight is obtained. The loss in weight is silica. Deduct a determined blank.

5. **Determination of Total Iron Oxide** (Volumetric).—

Reagents.—Hydrochloric acid, sp. gr. 1.18. 1–3 phosphoric acid. Potassium permanganate, 1% solution. Stannous chloride, 5% solution in 1–1

hydrochloric acid. Mercuric chloride, saturated solution. Approximately 0.05 N potassium dichromate. Diphenylamine indicator, 1% in concentrated sulfuric acid.

Procedure.—Oxidize the solution in which iron is to be determined with a few drops of potassium permanganate solution. Concentrate to 50–75 ml., add 10 ml. of hydrochloric acid, and bring to boiling. Reduce the iron by dropping in stannous chloride solution until the yellow color of the ferric chloride disappears. Not more than 2 or 3 drops should be added in excess. Cool the solution to room temperature. Add 10 ml. of a saturated mercuric chloride solution and stir thoroughly. A small white precipitate of mercurous chloride should form slowly, indicating that a slight excess of stannous chloride had been present. Allow to stand for a minute or two until no more precipitate appears to form. If the iron is high (15% or more) add 10 ml. of 1–3 phosphoric acid to suppress the ferric color at the end of the titration. Dilute to 150 ml. to 200 ml. and add 5 drops of diphenylamine indicator. Titrate with 0.05 N potassium dichromate. The point where the color changes to a deep blue, which does not fade on stirring, is taken as the end point. The final additions should be made slowly since there is a slight lag in the reaction. Deduct a blank of 0.1 ml.

6. Determination of Total Iron Oxide (Colorimetric).—

Reagents.—Potassium thiocyanate solution, 10%, or ammonium thiocyanate solution, 8%. Potassium permanganate solution, 1%. Standard ferric sulfate solution. Permanent standards.

Procedure.—Adjust the acidity of the solution in which iron is to be determined to 5% with sulfuric acid, and add potassium permanganate solution until faintly pink. Transfer to a 100 ml. Nessler tube (the volume at this stage should be approximately 100 ml.), add 10 ml. of potassium thiocyanate solution, and immediately gage the color, either by comparing with permanent standards or by titrating standard ferric solution into a duplicate tube containing 100 ml. of the blank solution and the same amount of thiocyanate solution as used in the sample. The comparison is best made in a camera. Deduct a determined blank. The sample solution, after developing the color, should not be exposed to bright light.

7. Determination of Ferrous Oxide.—

Reagents.—Approximately 0.05 N potassium dichromate. Diphenylamine indicator.

Procedure.—To the cold solution containing the ferrous iron, add 5 drops of diphenylamine indicator and titrate with 0.05 N potassium dichromate. The point where the color changes to a deep blue, which does not fade on stirring, is taken as the end point. Deduct a blank of 0.1 ml.

8. Determination of R_2O_3 and Alumina.—

Reagents.—Hydrochloric acid, sp. gr. 1.18. Ammonium hydroxide, sp. gr. 0.90. Methyl red indicator. Ammonium chloride wash solution.

Procedure.—Using methyl red as indicator, add ammonium hydroxide carefully to the hot solution containing the R_2O_3 until the color just changes to a distinct yellow. Allow to settle, filter, and wash four times with hot ammonium chloride wash solution. Return the precipitate to the beaker and dissolve by heating with 10 ml. hydrochloric acid and some water. Dilute, heat to boiling, and precipitate as before. Filter, police the beaker, and wash

well with hot ammonium chloride wash solution. Place the precipitate in a weighed crucible provided with cover. Dry, ignite carefully at first, finally heat to 1100° C. for an hour, cover, cool in a desiccator over activated alumina, and, as soon as cool, weigh quickly, keeping the crucible covered. Deduct a determined blank. The net weight represents combined oxides of aluminum, iron, titanium, zirconium, phosphorus, etc. For routine work the iron and titanium oxides are deducted and the balance considered to be alumina. For accurate work the remaining oxides should be determined and deducted.

9. Determination of Titanium Oxide.—

Apparatus.—Colorimeter. Duboscq, Kennicott-Campbell-Hurley, or any satisfactory type may be used.

Reagents.—1–1 sulfuric acid. Hydrogen peroxide, 3% solution. Standard titanic sulfate solutions, equivalent to 1.0, 0.10, 0.05 g. titanium dioxide per liter.

Procedure.—Transfer the solution containing the titanium oxide to a 100 ml. volumetric flask. Add 10 ml. of 1–1 sulfuric acid and 3 ml. of 3% hydrogen peroxide, fill to the mark with water, and mix. Compare with a standard solution of peroxidized titanium in a colorimeter.

In applying this instrument it is advisable and readily practicable to adjust several times on the same aliquot, approaching the matching point from the stronger and the weaker side in sequence, after which an average of the readings is taken.

In the absence of a colorimeter, place 10 ml. of 1–1 sulfuric acid in a duplicate Nessler tube, add 3 ml. of 3% hydrogen peroxide, and water to just below the mark. Add unperoxidized titanium solution to this tube until the color matches that of the sample, making the comparison with a camera.

10. Determination of Sodium Oxide.—

Reagents.—1–1 sulfuric acid. Zinc uranyl acetate reagent. Ethyl alcohol, 95%. Acetone. 0.1 N potassium permanganate. Potassium permanganate, 1% solution. Aluminum coil.

Procedure.—Cool the solution containing the soda (7 ml. volume), add 70 ml. zinc uranyl acetate reagent, and stir until precipitate forms. Let stand at least one-half hour, and filter through a 9 cm. filter, using a little pulp. Wash with reagent just enough times to transfer all of the precipitate from the beaker to the filter. Wash twice with 2 ml. portions of 95% ethyl alcohol, and five times with 2 ml. portions of acetone. Remove the excess acetone by suction or dry for a few minutes at 105° C. Wash the suction flask carefully and use it to receive the sodium zinc uranyl acetate which is washed through the filter with hot water. Transfer this solution to a 250 ml. beaker, add enough potassium permanganate to color the solution, and 30 ml. of 1–1 sulfuric acid. Place an aluminum coil in the beaker and boil for 30 minutes. When reduction is complete, cool, remove coil, rinse off with water, stir vigorously, and titrate with standard potassium permanganate. A blank must be carried through with the determination.

11. Determination of Calcium Oxide.—

Reagents.—Ammonium hydroxide, sp. gr. 0.90. Ammonium oxalate, saturated solution. 1–1 sulfuric acid. Approximately 0.018 N potassium permanganate.

Procedure.—Adjust the volume of the solution containing the calcium to approximately 100 ml. Heat to boiling, add a slight excess of ammonium hydroxide, and 10 ml. of ammonium oxalate solution. Heat just below the boiling point for 1 hour, keeping the solution alkaline. Cool, filter through a small, close-textured paper and wash 8 times with small portions of hot water. Puncture the paper and wash, with hot water, as much as possible of the precipitate into the beaker in which the precipitation was made. Pour 30 ml. of 1–3 sulfuric acid through the filter, and wash thoroughly. Heat to 80° to 90° C. and titrate at once with standard potassium permanganate solution. Deduct a determined blank.

12. **Determination of Magnesium Oxide.**—

Reagents.—Hydrochloric acid, sp. gr. 1.18. Ammonium hydroxide, sp. gr. 0.90. Diammonium phosphate, 10% solution. Ammonium nitrate wash solution.

Procedure.—Acidify the solution containing the magnesium with hydrochloric acid and add 10 ml. of diammonium phosphate solution. While stirring vigorously, slowly add 30 ml. of ammonium hydroxide. Allow to stand overnight. Filter and wash well with cold ammonium nitrate wash solution. Place the residue in a weighed porcelain or vitreosil crucible and ignite at 1100° C. until completely white. Weigh as magnesium pyrophosphate and deduct a determined blank.

Magnesium pyrophosphate $\times$ 0.3621 = magnesium oxide.

13. **Determination of Manganous Oxide.**—

Reagents.—Nitric acid, sp. gr. 1.42. Silver nitrate, 0.3% solution. Ammonium persulfate, 2% solution. Approximately 0.018 N sodium arsenite solution.

Procedure.—Adjust the volume of the solution containing the manganese to approximately 75 ml. Add 4 ml. nitric acid, 10 ml. silver nitrate solution, and 50 ml. of a warm, freshly prepared ammonium persulfate solution. Heat gently until the permanganic acid is fully developed and cool to room temperature. Titrate with the standard sodium arsenite solution.

Note.—If desired, the silver may be precipitated before the titration by adding 5 ml. of 0.2% solution of sodium chloride. If this is done, the same addition must be made during the standardization of the arsenite solution.

14. **Determination of Phosphorus Pentoxide.**—

Reagents.—Ammonium molybdate solution. Approximately 0.1 N sodium hydroxide. Approximately 0.1 N nitric acid. Nitric acid wash solution, 1%. Potassium nitrate wash solution, 1%. Phenolphthalein indicator.

Procedure.—Adjust the volume of the solution containing the phosphorus to not more than 150 ml., and the acidity to 5% with nitric acid. Heat to 40–50° C., add 50 ml. of ammonium molybdate reagent, stir well, and let stand till the precipitate has settled and no more appears to form. Filter, wash twice with nitric acid wash solution, then with potassium nitrate wash solution until the washings are no longer acid. Place the paper and residue in the flask, add a measured volume of 0.1 N sodium hydroxide, more than sufficient to dissolve the precipitate, and shake until the yellow color has disappeared. Add 2–3 drops of phenolphthalein solution and titrate immediately with the 0.1 N nitric acid to the disappearance of the pink color. Calculate the phos-

phorus pentoxide present from the net volume of 0.1 N sodium hydroxide necessary to dissolve the phosphomolybdate.

NOTES.—The determination is apparently not affected by small amounts of vanadium. For very accurate work, or if much vanadium is present, reduce it with ferrous sulfate, add a few drops of sulfurous acid, and about 8 g. of phosphorus-free ferric nitrate nonahydrate, to prevent subsequent reduction of the molybdenum. Cool to 10–20° C., add 50 ml. ammonium molybdate reagent, and continue as above.

After precipitation of ammonium phosphomolybdate, the determination may also be completed by weighing the precipitate after drying on a Gooch crucible, or by dissolving the precipitate in ammonium hydroxide, and precipitating the phosphorus as magnesium ammonium phosphate.

15. **Determination of Vanadium.**—

Reagents.—1–1 sulfuric acid. Hydrogen peroxide, 3% solution. Standard vanadium sulfate solution equivalent to about 0.0001 g. vanadium sesquioxide per ml.

Procedure.—Concentrate the solution containing the vanadium to a little less than 100 ml., cool, and adjust the acidity to approximately 2.5% with sulfuric acid. Transfer to a 100 ml. Nessler tube. In a duplicate tube, place 5 ml. of 1–1 sulfuric acid and dilute to 100 ml. If the sample has a faint yellow tinge, match it by mixing a little ferric sulfate solution with the blank. Add 3 ml. of 3% hydrogen peroxide to each tube and mix. Allow the sample to stand 2 minutes, as there is a lag in the development of the color. By means of a standard vanadium sulfate solution, bring the color of the blank to the same depth as that of the sample, thus obtaining a measure of the vanadium oxide present. Comparison is made in a camera.

16. **Determination of Zirconium Oxide.**—

Reagents.—1–1 sulfuric acid. Hydrogen peroxide, 3% solution. Diammonium phosphate, 10% solution. Ammonium nitrate wash solution, 5%.

Procedure.—Adjust the volume of the solution containing the zirconium to 100–125 ml. Add 30 ml. of 1–1 sulfuric acid, 3 ml. of hydrogen peroxide, 10 ml. diammonium phosphate solution, and allow to stand overnight at 50–60° C. Filter on a close-textured paper and wash with a slightly acid cold ammonium nitrate wash solution. Ignite in a porcelain crucible at 500° C. until the carbon is completely burned off, finish the ignition at 1000° C., and weigh as zirconium pyrophosphate.

Zirconium pyrophosphate × .4645 = zirconium oxide.

ANALYSIS OF BAUXITE [20]

2. *A*. **Determination of Moisture.**—

Procedure.—Use a 10 g. sample and proceed as in Determination of Moisture—2, p. 19.

3. *A*. **Determination of Loss on Ignition.**—

Procedure.—Use a 1 g. sample and proceed as in Determination of Loss on Ignition—3.

4. *A*. **Determination of Silica.**—

Reagents.—No. 1 acid mixture. 1–1 sulfuric acid. Potassium pyrosulfate.

[20] Reference is made to numbered sections of the preceding procedures for the analysis of ore, in the subsequent procedures.

Procedure.—Decompose 1 g. of the dried sample in a medium sized casserole or Pyrex beaker by the addition of 60 ml. of No. 1 acid mixture. Cover, heat so as to concentrate slowly, and proceed as in the Determination of Silica—4.

NOTE 1.—If alumina, iron oxide, and titanium oxide are to be determined, bring into solution the material left from the hydrofluoric acid treatment by fusing thoroughly with about 1 g. of potassium pyrosulfate. Cool, dissolve the melt in a little water containing about 5 ml. of 1-1 sulfuric acid, heat to boiling and precipitate platinum by passing a rapid stream of hydrogen sulfide through the solution for 5 minutes. Filter and wash with hot water. Boil the filtrate thoroughly to expel hydrogen sulfide and combine this solution with the main solution in 250 ml. volumetric flask. Fill to the mark when cool and mix.

NOTE 2.—For routine work the fusion and platinum removal may be omitted.

4. *B*. **Determination of Silica in Calcined Bauxite.**—

Reagents.—Fusion mixture. 1-1 sulfuric acid. Potassium pyrosulfate. Alcoholic methyl chloride.

Procedure.—Fuse 1 g. of sample in a 40 ml. platinum crucible with 6 g. fusion mixture. Complete decomposition should be obtained in about 20 minutes. Cool, place the crucible in a large platinum dish, and leach with a small amount of hot water till the melt is well broken up. Add 30 ml. of 1-1 sulfuric acid and proceed as in the Determination of Silica—4.

NOTE 1.—Bring into solution any appreciable amount of material left from the hydrofluoric acid treatment by fusing thoroughly with about 1 g. of potassium pyrosulfate. After cooling, dissolve the melt in a little water containing 5 ml. of 1-1 sulfuric acid. Combine this solution with the main solution, heat to boiling and precipitate platinum by passing a rapid stream of hydrogen sulfide through the solution for 5 minutes. Filter, and wash with hot water. Boil the filtrate thoroughly to expel hydrogen sulfide, and transfer to a 250 ml. volumetric flask. Fill to the mark when cool and mix.

NOTE 2.—Sodium borate, if not removed from the silica by thorough washing, will cause an error due to the volatilization of boron as boron trifluoride. For this type of analysis it has been demonstrated that the silica can be washed sufficiently clean to make the error from this source negligible. However, if alumina is to be determined and not obtained by difference, subtracting the sum of the percentages of loss on ignition and the impurities from 100, the sodium borate must be removed. This is accomplished as follows: Place the sodium carbonate-borax fusion in a large porcelain or platinum dish, cover the dish, and treat with the alcoholic methyl chloride solution. When effervescence ceases, remove the cover and heat just below the boiling point, preferably on a water bath, in a good hood. Cleanse the crucible and add its contents to the dish. Add more reagent as necessary until solution is complete, boil to a small volume, and evaporate to dryness on the bath. To remove the last traces of boron, evaporate to dryness at 80° to 85° C. on the bath two or three times with successive additions of small portions of the reagent, taking care to wash down the sides of the dish.

5. *A*. **Determination of Total Iron Oxides.**—

Procedure.—Pipette 100 ml. of the 250 ml. silica filtrate solution into a beaker and proceed as in Determination of Total Iron Oxide—5.

7. *A*. **Determination of Ferrous Oxide.**—

Reagents.—1-1 sulfuric acid.

Procedure.—Place 2 g. of sample in a 250 ml. Erlenmeyer flask, add 15 ml. of 1-1 sulfuric acid and 45 ml. of water. Heat to boiling and continue boiling gently for 10 minutes. Cool and proceed as in the Determination of Ferrous Oxide—7.

8. *A*. **Determination of R_2O_3 and Alumina.—**

Reagents.—Hydrochloric acid, sp. gr. 1.18.

Procedure.—Pipette 100 ml. of the 250 ml. silica filtrate solution into a beaker. Add 10 ml. of hydrochloric acid, dilute to about 150 ml., heat to boiling, and proceed as in the Determination of R_2O_3 and Alumina—8.

9. *A*. **Determination of Titanium Oxide.—**

Procedure.—Pipette 25 ml. of the 250 ml. silica filtrate solution into a 100 ml. volumetric flask and proceed as in the Determination of Titanium Oxide—9.

11. *A*. **Determination of Calcium Oxide.—**

Reagents.—Sodium carbonate, anhydrous. Sodium borate, anhydrous. Hydrochloric acid, sp. gr. 1.18. 1–1 hydrochloric acid. Ammonium hydroxide, sp. gr. 0.90.

Procedure.—Mix 2 g. of the sample with 10 g. of anhydrous sodium carbonate and 1.5 g. of anhydrous sodium borate. Heat gradually till the water has been driven out, then increase the temperature to 1000–1100° C. and continue till the fusion becomes quiet. Cool in a thin layer and leach in about 150 ml. hot water until the melt is well broken up. Filter, and wash twice with hot sodium carbonate wash solution. Puncture the paper and wash the residue into the beaker used for the extraction. Wash the paper with 20 ml. 1-1 hydrochloric acid, followed by hot water. Boil the solution for a few minutes, and neutralize the acid with ammonium hydroxide, using methyl red as indicator. Filter and wash 5 times with ammonium chloride wash solution. Return the precipitate with the paper to the beaker, dissolve in 10 ml. hydrochloric acid, and dilute with a little hot water. Heat to boiling and precipitate again with ammonium hydroxide. Filter and wash as before. Evaporate the combined filtrates to dryness and heat to about 500° C. to expel ammonium salts. Cool, dissolve the residue in 2 ml. hydrochloric acid and a little water, filter and wash. The volume of the filtrate should be about 100 ml. Proceed as in the Determination of Calcium—11.

12. *A*. **Determination of Magnesium Oxide.—**

Reagents.—Hydrochloric acid, sp. gr. 1.18. Ammonium hydroxide, sp. gr. 0.90. Ammonium persulfate, crystal.

Procedure.—Heat the filtrate from the calcium determination, add 2 ml. excess ammonium hydroxide and 0.5 g. ammonium persulfate, and boil till any manganese present is well coagulated. Filter and wash. Evaporate the filtrate to dryness and heat to 500° C. to volatilize all ammonium salts. Cool, and dissolve the residue in 2 ml. hydrochloric acid and a little hot water. Heat to boiling, neutralize with ammonium hydroxide, filter, and wash with hot ammonium chloride wash solution. Proceed as in the Determination of Magnesium Oxide—12.

13. *A*. **Determination of Manganous Oxide.—**

Reagents.—No. 1 acid mixture.

Procedure.—Place 1–2 g. of the sample in a beaker or casserole and add 50–70 ml. of acid mixture No. 1. Evaporate until fumes of sulfuric acid are evolved, and continue fuming for some time. Cool, cautiously add 125 ml. water, and heat until all soluble salts are in solution. Filter off the silica and wash thoroughly. Proceed as in the Determination of Manganous Oxide—13.

14. *A*. **Determination of Phosphorus Pentoxide.—**

Reagents.—Nitric acid, sp. gr. 1.42. 1–1 nitric acid. Hydrofluoric acid, 48%. Sodium carbonate, anhydrous.

Procedure.—To 2 g. of finely ground sample in a platinum dish add 60 ml. of 1–1 nitric acid and enough hydrofluoric acid to completely decompose the silica and silicates. 10 ml. will suffice for ordinary bauxite. Evaporate to dryness at a moderate heat. Evaporate 2 or 3 times more with 50 ml. of 1–1 nitric acid only, to remove all hydrofluoric acid. Finally digest with 15 ml. of nitric acid and 100 ml. of water, filter, and wash a few times. Fuse the residue with 1 to 3 g. of sodium carbonate, cool and add the melt to the main solution. Proceed as in the Determination of Phosphorus Pentoxide—14.

NOTES.—The determination is apparently not affected by small amounts of vanadium. For very accurate work, or if much vanadium is present, reduce it with ferrous sulfate, add a few drops of sulfurous acid, and about 8 g. of phosphorus-free ferric nitrate nonahydrate, to prevent subsequent reduction of the molybdenum. Cool to 10–20° C., add 50 ml. ammonium molybdate reagent, and continue as before.

After precipitation of ammonium phosphomolybdate, the determination may also be completed by weighing the precipitate after drying in a Gooch crucible, or by dissolving the precipitate in ammonium hydroxide, and precipitating the phosphorus as magnesium ammonium phosphate as described in detail elsewhere in these methods. This is the most accurate process.

15. *A*. **Determination of Vanadium Oxide.**—

Reagents.—Sodium hydroxide, pellets. Sodium hydroxide solution, 3%. 1–1 sulfuric acid.

Procedure.—Fuse 3 g. of sample with 6 g. of sodium hydroxide in an iron crucible, raising the heat cautiously to avoid loss as dust. Finally hold at a high temperature for 20 minutes. Cool, dissolve by heating with 75 ml. of water, filter through a paper previously washed with 3% sodium hydroxide solution and wash twice. Pass carbon dioxide into the filtrate till a fairly thick precipitate has formed, which is, however, only a portion of the aluminum. Filter through a paper washed with 3% sodium hydroxide solution, wash the residue twice, and pour the filtrate into 20 ml. of 1–1 sulfuric acid. Proceed as in the Determination of Vanadium Oxide—15.

ANALYSIS OF CALCINED ALUMINA

1. *A*. **Preparation of Sample.**—Mix well the portion of alumina collected, and quarter down to the amount which it is wished to reserve for the determination of impurities, ordinarily about 4 ounces. Reserve a separate part for mesh test and loss on ignition. Quickly sift the 4 ounce lot through a 50-mesh sieve, grind the part retained till it passes the sieve, and thoroughly remix. During the grinding, cover the coarse particles with a little of the sifted alumina to prevent loss, and rinse the mortar with some more of this fine part. Further grinding of the main sample is accompanied by danger of disproportionate contamination, and is, therefore, omitted.

3. *A*. **Determination of Loss on Ignition.**—Use a 1 g. sample and proceed as in the Determination of Loss on Ignition—3.

4. *D*. **Determination of Silica.**—

Reagents.—Potassium sulfate (special, low silica and iron). Sulfuric acid, sp. gr. 1.84. Potassium permanganate solution, 1%.

Procedure.—Place 42 g. of potassium sulfate and 12 ml. of concentrated sulfuric acid (equivalent to 60 g. of potassium bisulfate) in a 100 ml. platinum crucible. Place 5 g. of sample on top of the fusion mixture and heat at first gently with the cover on the crucible, using a low flame. Then increase the heat till the full flame of the burner is used. If, after the fusion has quieted down, there is a little unattacked sample, proceed as follows: Cool the melt on the sides of the crucible by carefully rotating the contents. Add 1 ml. of concentrated sulfuric acid from a dropping bottle, dropping the acid around the sides of the crucible. Re-fuse as before and while cooling run the melt up on the sides of the crucible. Transfer the melt to a 600 ml. beaker and add 40 ml. of concentrated sulfuric acid. Heat until the melt is completely broken up and copious fumes are evolved. Cool, and cautiously add about 500 ml. of hot water. Heat, with stirring, to complete solution of soluble salts. Filter off the silica, and wash with a small amount of hot water. Set aside the concentrated filtrate and wash the silica thoroughly. Proceed with the ignition and volatilization as in the Determination of Silica—4.

Pass hydrogen sulfide for 20 minutes through the filtrate from the silica, heat to coagulate the precipitated sulfides, filter, and wash. Boil the filtrate to remove hydrogen sulfide, cool, and add potassium permanganate solution dropwise till a pink color persists for a minute or two. Dilute to 500 ml. in a volumetric flask.

6. *A*. **Determination of Ferric Oxide.**—

Procedure.—Transfer 100 ml. of the silica filtrate solution to a 100 ml. Nessler tube, and proceed as in the Determination of Ferric Oxide—6.

NOTES.—If the sample gives too deep a color to match readily, use a smaller aliquot, or precipitate iron and titanium together with cupferron. Details of this procedure will be found in the section on preparation of standard titanium solution. Deduct the titanium oxide from the total oxides.

The amount of thiocyanate used for the sample must agree closely with that used when adjusting the permanent standards or titrating the temporary one.

The sample solution, after developing the color, should not be exposed to bright light.

9. *B*. **Determination of Titanium Oxide.**—

Reagents.—Hydrogen peroxide, 3%. Standard titanium solution, equivalent to 0.0001 g. of titanium dioxide per ml. Dilute the unperoxidized solution used for this determination in bauxite.

Procedure.—Place 200 ml. of the prepared filtrate from the silica determination in a 200 ml. Nessler tube, add 5 ml. of hydrogen peroxide, and mix. Compare with a scale of standards or match by titrating standard titanium solution into a duplicate tube containing 200 ml. of the blank solution and 5 ml. of hydrogen peroxide.

10. *A*. **Determination of Sodium Oxide.**—

Reagents.—Hydrofluoric acid, 48%. 1–1 ammonium hydroxide. Sulfuric acid, sp. gr. 1.84.

Procedure.—To a large platinum dish add 1 g. sample, 20 ml. concentrated hydrofluoric acid, and 20 ml. of water. Then add 50 ml. of 1–1 ammonium hydroxide and evaporate to fumes. Heat under the Dutch oven until dry. Repeat the fuming using one-half quantities of the hydrofluoric acid and ammonium hydroxide. Fume until almost dry but still moist and fuming. Add

5 ml. of concentrated sulfuric acid, and fume till all fumes are driven off. Ignite at dull red heat. Add 5 ml. concentrated sulfuric acid and fume until all fumes are driven off. Add 2 ml. of concentrated sulfuric acid, and fume for a few minutes, but do not drive off all the acid. Leave about 1 ml. of sulfuric acid. It is important that the fuming is not carried to dryness, as an insoluble residue may be formed with the fixation of some soda. Add 50 ml. of hot water, evaporate to 7 ml., and proceed as in the Determination of Soda—10.

$$1 \text{ ml. } 0.1 \text{ N } KMnO_4 = 0.000515 \text{ g. } Na_2O.$$

ANALYSIS OF ALUMINUM HYDRATE

1. *B*. **Preparation of Sample.**—Take the sample from a carload lot with a tube sampler. Push the tube down through the hydrate to the bottom of the car, turn the inner tube so that the slot will coincide with the slot in the outer tube, and jar the tube so that it will fill with hydrate. Withdraw the tube and empty the hydrate into a bucket. Take samples at 12 points evenly distributed over the car. Immediately reduce by a sample divider to about 1 pound, and preserve in a glass Mason jar, sealed with a rubber ring. The analysis should be made at once.

3. *B*. **Determination of Loss on Ignition.**—Use a 1 g. sample and proceed as in the Determination of Loss on Ignition—3.

NOTE.—Much care is necessary when starting to heat the hydrate. If it is heated too rapidly, the high rate at which moisture is driven off will force the particles of hydrate out of the crucible.

4. *E*. **Determination of Silica.**—

Reagents.—Sulfuric acid, sp. gr. 1.84.

Procedure.—Weigh a 10 g. sample into a casserole. Add enough water to make a thin paste, then 25 ml. sulfuric acid, and cover the casserole. When the mixture is heated slightly, violent action takes place between the hydrate and the acid to form aluminum sulfate. After this reaction, continue to heat to strong fuming, and proceed as in the Determination of Silica—4.

6. *B*. **Determination of Ferric Oxide.**—

Reagents.—1-1 sulfuric acid.

Procedure.—Weigh 1 to 5 g. of sample, depending on the percentage of ferric oxide supposed to be present, so as to give 0.0001 to 0.0003 g. ferric oxide. Place in a 200 ml. beaker and add, according to the size of the sample, 15 to 25 ml. of 1-1 sulfuric acid. Mix, then heat for 20–30 minutes, stirring occasionally to prevent caking. Cool somewhat, add a little cold water, dilute to about 70 ml. with hot water, boil till clear, filter, and wash. The volume of filtrate and washings should not exceed 90 ml. Add potassium permanganate solution till the pink color lasts for a minute. Cool and transfer to a 100 ml. Nessler tube. Proceed as in the Determination of Ferric Oxide—6.

10. *B*. **Determination of Sodium Oxide.**—

Reagents.—Sulfuric acid, sp. gr. 1.84.

Procedure.—Place 1 g. of the sample in a 250 ml. beaker and moisten with water. Heat and add 2.5 ml. of sulfuric acid. Continue heating until most

of the acid is driven off. Add 8 ml. of water and heat to solution of salts. Proceed as in the Determination of Sodium Oxide—10.

17. **Determination of Insoluble Matter.—**

Reagents.—2–1 sulfuric acid.

Procedure.—Weigh a 10 g. sample into a casserole, add 50 ml. 2–1 sulfuric acid, and boil until solution is clear, but not until fumes are evolved. Dilute, filter, wash thoroughly, and ignite the residue in platinum for 1 hour at 1000° C. Cool and weigh. Weight of residue represents insoluble matter.

REAGENTS AND STANDARD SOLUTIONS

No. 1 Acid Mixture.—485 ml. of water, 115 ml. of concentrated sulfuric acid, 200 ml. of concentrated hydrochloric acid, 200 ml. of concentrated nitric acid.

No. 2 Acid Mixture.—200 ml. water, 400 ml. concentrated sulfuric acid, 400 ml. concentrated nitric acid.

Fusion Mixture.—Mix 5 parts by weight of anhydrous sodium carbonate with 1 part of anhydrous sodium borate.

Alcoholic Methyl Chloride.—Pass dry hydrogen chloride into cooled methyl alcohol for 1 to 2 hours.

Approximately 0.05 N Potassium Dichromate.—Dissolve about 2.5 g. of crystals per liter of solution desired. Standardize against a Bureau of Standards standard sample of Sibley Iron Ore in the following manner: Dissolve 0.2 g. of the ore in 25 ml. 1–1 hydrochloric acid, and heat at a temperature below the boiling point, until the solution has evaporated to a sirupy consistency. Add 50 ml. hot water and 10 ml. hydrochloric acid, and bring to boiling. Reduce the iron by dropping in stannous chloride solution until the yellow color of the ferric chloride disappears. Not more than 2 or 3 drops should be added in excess. Cool the solution to room temperature. Add 10 ml. of a saturated mercuric chloride solution and stir thoroughly. A small white precipitate of mercurous chloride should form slowly, indicating that a slight excess of stannous chloride had been present. Allow to stand for a minute or two until no more precipitate appears to form. Add 10 ml. of 1–3 phosphoric acid, dilute to 150–200 ml., and add 5 drops of diphenylamine indicator. Titrate with the dichromate solution until the color changes to a deep blue, which does not fade on stirring. The final additions of dichromate should be made slowly, since there is a slight lag in the reaction. Deduct a 0.1 ml. blank. Calculate the ferric oxide value per ml. of the dichromate.

Standard Ferric Sulfate Solution.—Equivalent to 0.0001 g. ferric oxide per ml. Dissolve 0.4912 g. of ferrous ammonium sulfate in water containing 25 ml. of 1–1 sulfuric acid, add potassium permanganate solution until the iron is just oxidized, and dilute to 1 liter.

Standard Titanic Sulfate Solutions.—Equivalent to 1.0, 0.10, 0.05 g. titanium dioxide per liter. For the first, weigh out a little more than 1 g. of titanium oxide, mix with 10 g. of sodium carbonate in a platinum crucible, and fuse thoroughly. Extract the melt with hot water, filter, and wash the residue. Transfer the bulk of this residue to a beaker, add 50 ml. sulfuric acid, and heat strongly to dehydrate any silica. Cool, dilute to 300 ml., heat until soluble salts are dissolved, then filter, and dilute the filtrate to 1 liter in a volumetric flask. In standardizing the solution, provision must be made for iron. If it is very low, it may be determined colorimetrically with thiocyanate, and the proper deduction made, but if much is present, it should be removed by the procedure next described. Pipette 25 ml. into a beaker. If iron is to be separated, dilute to 100 ml. and add 1 g. tartaric acid. Saturate with hydrogen sulfide, then make distinctly ammoniacal, and continue the passage of hydrogen sulfide into the solution for a few minutes. Filter off the iron sulfide and wash with a solution containing 10 ml. of ammonium sulfide solution prepared by adding 200 ml. ammonium hydroxide to 800 ml. water, and saturating with hydrogen sulfide and 10 g. ammonium chloride per liter. Boil the filtrate for a short time, then neutralize with 1–1 sulfuric acid and add 10 ml. excess. Continue boiling till all hydrogen sulfide has been removed. Dilute this filtrate, or, if not treated for iron, the original 25 ml. to 300 ml., including 25 ml. hydrochloric acid. Cool in ice and stir in ice-cold, filtered cupferron solution (preferably prepared from recently recrystallized material) until the precipitate coagulates well, and no more forms on further addition of the reagent. About 50 ml. of 4% solution should suffice. Filter and wash with cold 1–10 hydrochloric acid containing a little cupferron until the washings are free from sulfates. Dry the precipitate and ignite in a weighed crucible, provided with a cover. Heat gently at first, then at 1100° C. for 45 minutes. Cover the crucible, cool in a desiccator over activated alumina, and weigh quickly as soon as cool. It is advisable to repeat the ignition for a short time and check the weight. If iron was not separated, deduct the iron oxide content, as determined by the thiocyanate method. The residue is titanium dioxide. Calculate the titanium dioxide value of the solution. It will be very nearly 1 mg. per ml. This solution may be used for titration when samples high in titanium are to be compared in a camera.

For titration, when samples low in titanium are to be compared in a camera, a strength of 0.1 g. titanium dioxide per liter is preferable. To prepare this, dilute the stronger solution with an appropriate amount of 5% sulfuric acid. For comparison in the colorimeter, a peroxidized solution containing 0.05 g. titanium dioxide per liter is used. To the necessary amount of strong solution add sufficient sulfuric acid and 3% hydrogen peroxide so that the final solution will contain 5 ml. of sulfuric acid, and 3 ml. of 3% hydrogen peroxide in each 100 ml. Potassium titanium fluoride is also recommended as the starting material for this solution. The appropriate treatment is fully described by Hillebrand and Lundell in "Applied Inorganic Analysis," page 458.

Approximately 0.018 N and 0.1 N Potassium Permanganate Solution.—Dissolve crystallized C.P. potassium permanganate in a small amount of distilled water, using about 0.573 g. (0.018 N) and 3.11 g. (0.1 N) for each liter of diluted solution desired. It should be allowed to stand for several days, then filtered through purified asbestos before making up to the final volume. The finished solution (0.018 N) will correspond to approximately 0.0005 g. calcium oxide per ml. Keep in a glass-stoppered (preferably amber-glass) bottle in a dark place. To standardize the solution, dry some C.P. grade sodium oxalate at 105° C. for an hour. Dip out about 0.05 g. for the weak solution and a proportionally larger amount for the strong solution. Weigh exactly, and dissolve in 100 ml. of warm water. Add 15 ml. of 1–1 sulfuric acid, heat to 80–90° C., then, using a burette with glass stopcock, titrate with the potassium permanganate solution. Deduct the blank required for a similar amount of hot water and acid. Calculate the sodium oxalate oxidized per ml. of permanganate, and multiply this value by 0.4814 to obtain the equivalent calcium oxide value.

Standard Vanadium Sulfate Solution.—Equivalent to about 0.001 g. vanadium sesquioxide per ml. Dissolve 1.561 g. ammonium metavanadate in 50 ml. 1–1 sulfuric acid. Add 200 ml. of water, and weak permanganate solution till a faint pink color persists for a few minutes. Dilute to 1 liter with water. Dilute a 50 ml. portion to 100–150 ml., heat to above 70° C., and add dilute potassium permanganate solution till a faint pink color persists for at least a minute. Keep the solution hot and stir occasionally until the pink color disappears, then cool. Add 2 drops of diphenylamine indicator prepared by dissolving 1 g. of diphenylamine in 100 ml. sulfuric acid. From a burette add ferrous solution in slight excess, shown by the disappearance of the deep blue color, leaving a light green. Titrate back to the deep blue with the standard dichromate solution. Measure out the same amount of ferrous solution as was used, add 10 ml. of 1–1 sulfuric acid and dilute to 100–150 ml. Add indicator and titrate with the potassium dichromate solution. The difference between this and the preceding back titrations is the dichromate consumed in oxidizing from the tetravalent to the pentavalent state the vanadium in the 50 ml. portion of vanadium solution. Calculate from this the vanadium sesquioxide value of the latter solution per ml. To find the vanadium content, reduce a 50 ml. portion with an excess of ferrous ammonium sulfate and titrate back with dichromate, using diphenylamine as indicator. The 0.05 N dichromate solution used in the iron oxide determinations may be conveniently used. The vanadium sesquioxide factor = ferric oxide factor $\times$ 0.9389. An approximately 0.05 N ferrous ammonium sulfate solution may be prepared by dissolving 20 g. of ferrous ammonium sulfate hexahydrate crystals in water containing 25 ml. of 1–1 sulfuric acid, and diluting to 1 liter.

Standard Sodium Arsenite Solution.—For the stock solution, dissolve 10 g. arsenic trioxide and 30 g. sodium carbonate in a small amount of hot water, filter, and dilute to 1 liter. For the standard solution, dilute the required amount of stock solution (about 50 ml.) to 1 liter. This will be equivalent to about 0.0002 g. manganous oxide per ml. After 24 hours, standardize against a standard manganese alloy containing about 1% manganese, by dissolving 0.2 g. of the latter in 30 ml. acid mixture No. 2 and carrying through procedure 13.

Approximately 0.1 N Sodium Hydroxide Solution.—Prepare a 50% solution of sodium hydroxide and allow it to stand, protected against the introduction of carbon dioxide, until the carbonate has settled out. Dilute about 5.5 ml. of this solution to 1 liter with freshly boiled water, and preserve in a bottle provided with a guard tube to prevent access of air. The solution is standardized by titrating with the 0.1 N nitric acid.

Approximately 0.1 N Nitric Acid Solution.—Dilute 6.5 ml. of nitric acid to 1 liter. Standardize by titrating sodium carbonate prepared by heating pure sodium bicarbonate at 260–265° C. for 30 minutes, using methyl yellow indicator.

Ammonium Molybdate Solution.—Mix 65 g. of ammonium molybdate, 225 g. of ammonium nitrate, 40 ml. of ammonium hydroxide, and 600 ml. of water. Heat gently. When crystals are all in solution, filter, and without washing, dilute to 1 liter.

Uranyl Zinc Acetate.—*Solution A.* Uranyl acetate 10 g., acetic acid (30%) 6 g., water to make 65 g. *Solution B.* Zinc acetate ($3H_2O$) 30 g., acetic acid (30%) 3 g., water to make 65 g. After the salts in *A* and *B* are dissolved by warming, the solutions are mixed, a few mg. of sodium chloride added, and the solution is allowed to stand 24 hours. The solution is filtered immediately before it is to be used.

Diphenylamine Indicator.—Dissolve 1 g. in 100 ml. of sulfuric acid, and shake until solution is complete. It should be replaced after 2 or 3 months, since the color change produced by old solution is less pronounced.

Methyl Red Indicator. Dissolve 1.0 g. of crystals in a few ml. of ammonium hydroxide, dilute to 1 liter, and add hydrochloric acid until neutral. Avoid addition of sufficient acid to reprecipitate the crystals.

Methyl Yellow.—Dissolve 0.1 g. in 100 ml. of 90% alcohol. 1 drop indicator is used per 10 ml. solution.

Phenolphthalein Indicator.—Dissolve 0.5 g. of solid phenolphthalein in 50 ml. of 95% ethyl alcohol, and dilute to 100 ml.

Ammonium Chloride Wash Solution.—Dilute 25 ml. of hydrochloric acid, neutralize to methyl red with ammonium hydroxide, and dilute to 1 liter. Add 2 drops excess of ammonium hydroxide.

Ammonium Nitrate Wash Solution.—Mix 900 ml. of water with 40 ml. nitric acid and 100 ml. of ammonium hydroxide.

ANALYSIS OF ALUNDUM [21]

Preparation of the Sample.—If the sample is of uniform composition the amount desired to work on is taken without any preparation. If it is not uniform, the entire sample must be crushed to small sized grains and the working sample selected by thorough mixing and quartering. The sample selected must *all* be put through a 60-mesh screen, using a hardened steel mortar for pulverizing.

The pulverized sample is repeatedly stirred with either a horseshoe or electro-magnet until all magnetic material is removed. If this magnetic

[21] Method used by the Norton Company; courtesy of M. O. Lamar.

material is to be weighed and determined, it too must be treated repeatedly with the magnet to free it entirely of the alundum which clings to it.

Fusion of the Sample.—Weigh 2.000 grams of the pulverized sample into a 30 ml. or larger platinum crucible and fuse with eight grams of a mixture of equal parts of anhydrous sodium carbonate and anhydrous borax. The sample should be mixed thoroughly with the larger part of the fusion mixture and covered with the remainder. Start the fusion with just enough heat to redden the bottom of the crucible and when fusion is well under way increase the heat to the full flame of a Bunsen burner. Finally fuse for 45 minutes with the full heat of a Fisher burner. Remove the heat, spread the fusion on the sides of the crucible in as thin a layer as possible, and allow to cool.

Determination of Silica.—Place the crucible and cover in 80 ml. of 1 : 3 H_2SO_4 contained in a 350 ml. casserole or 400 ml. beaker and boil gently until the fusion is completely dissolved. Remove the crucible and cover, rinsing any solution adhering to them back into the beaker, and evaporate the solution to fumes of H_2SO_4. The casserole or beaker should be covered with a glass triangle and watch glass and the boiling should not be so rapid as to cause spattering.

When the beaker and contents have cooled, add 125 ml. of water and boil until all salts have dissolved. Filter while hot through a 9 cm. S & S White Ribbon paper, or its equivalent. Be sure all the silica is transferred from the casserole or beaker to the filter paper, and when this is done wash the paper and precipitate 10–12 times with hot water. Transfer the paper and precipitate to a platinum crucible, smoke off the paper and ignite the crucible for 15 minutes at full heat of a Bunsen burner. Cool the crucible in a desiccator and weigh it. Add two drops of 1 : 1 H_2SO_4 and 2 or 3 ml. of HF. Evaporate the acids, ignite, cool, and weigh the crucible again. The difference between the two weights is silica and as a 2-gram sample is always taken, this figure multiplied by 50 gives the percentage of silica.

Fuse the residue in the crucible with 2 or 3 grams of potassium bisulphate, dissolve the fusion in the minimum amount of 1 : 3 H_2SO_4 and add the solution to the filtrate from the silica.

Separation of Iron, Titanium, Zirconium, Magnesium, Calcium, and Manganese from Cr, V, Al, and P_2O_5.—The filtrate from the silica determination (*A*) is concentrated to about 150 ml., cooled and almost neutralized with a concentrated solution of NaOH of the purest available quality. No indicator is used and the analyst simply adds the NaOH dropwise toward the end of the neutralization until vigorous stirring just re-dissolves the precipitate formed. Pour the nearly neutral solution (*A*) into 150 ml. of cold 15% NaOH containing also one gram each of Na_2CO_3 and Na_2O_2. Rinse out the beaker twice and add to the solution. Place on the steam bath and heat for one hour. Iron, titanium, and zirconium are precipitated as hydroxides, lime and magnesia as carbonates, and Cr is oxidized to chromate and goes into solution with Al, V, and P_2O_5. Cool and filter through a paper which has been treated with NaOH of the same strength. (This treatment of the paper will prevent the extraction of coloring matter from it.) Wash the precipitate (*B*) several times with a 1% solution of Na_2CO_3. Reserve the filtrate (*C*).

Dissolve the precipitate (*B*) in 25 ml. of hot 1 : 2 HCl and wash the paper thoroughly with hot 1% HCl. Dilute to about 150 ml., heat to boiling, add a

few drops of methyl red and wash the precipitate with hot 2% NH_4Cl solution, re-dissolve in dilute HCl and precipitate with ammonia with the same precautions. Wash the precipitate with hot 2% NH_4Cl. The precipitate (*D*) contains Fe, Ti, and Zr. The filtrates from both NH_4OH precipitations are combined into one solution (*E*) after evaporating them to a volume of about 125 ml. Reserve for lime, magnesia, and manganese.

Separation of Fe from Ti and Zr.—Dissolve the precipate (*D*) in hot dilute HCl, add 4 grams of tartaric acid, dilute with water to 150 ml. and neutralize with NH_4OH. Now add 2 ml. of concentrated HCl for each 100 ml. of volume, heat to boiling and saturate with H_2S. Let the solution cool, and preferably after standing overnight, filter off any platinum sulphide which may have been derived from the crucible. Wash the platinum sulphide with 1% H_2SO_4, saturated with H_2S and discard the paper. Make the filtrate alkaline with NH_4OH and pass in H_2S for 5 minutes. Let the precipitate stand for 30 minutes and filter through a close texture paper. Wash the precipitate (*F*) with a 5% ammonium sulphide solution containing also 2% NH_4Cl. Reserve the filtrate (*G*) for the determination of titanium and zirconium.

DETERMINATION OF IRON

(*a*) **Gravimetric Method.**—Place the paper containing the precipitate (*F*) of iron sulphide in the beaker in which the FeS precipitation was made and cover with a watch glass. Add 20–30 ml. of concentrated HNO_3 and 5 ml. of concentrated H_2SO_4. Heat on the hot plate to the complete destruction of all organic matter and evaporate to strong fumes of SO_3. It may be necessary to add a few more drops of concentrated HNO_3 to destroy the last traces of filter paper. Cool, dilute to 100–200 ml. (depending upon the amount of Fe present), heat to boiling and precipitate with a slight excess of ammonia. Add a little macerated filter paper pulp, filter and wash with hot 2% NH_4Cl. Ignite and weigh as Fe_2O_3. Discard the filtrate. In very careful work the Fe_2O_3 after ignition and weighing should be corrected for SiO_2 by treatment with HF and a few drops of H_2SO_4, evaporation to dryness and finally heating to 950° C.

(*b*) **Volumetric Method.**—Destroy the filter paper just as in the gravimetric method. Dissolve, after evaporation to SO_3 and cooling, in 1 : 3 HCl, heat to boiling, reduce with $SnCl_2$ and titrate the excess of $SnCl_2$ and all the reduced iron electrometrically using N/100 or N/10 $K_2Cr_2O_7$, depending on the amount of Fe present.

DETERMINATION OF Ti AND Zr

The filtrate (*G*) contains the titania and zirconia. Neutralize it in a covered beaker with H_2SO_4 and dilute to 200 ml. Add 20 ml. of concentrated H_2SO_4, boil out the H_2S and cool to 5–10° C. Precipitate Ti and Zr with a cold 4% solution of "cupferron," add the cupferron until a white milkiness is produced which disappears on stirring. Add macerated filter paper pulp and filter with suction, washing the precipitate about 15 times with dilute 1 : 10 HCl. Char the paper very cautiously in a weighed crucible. Finally ignite to constant weight, and weigh as "TiO_2 plus ZrO_2." Fuse the weighed precipitate with a small amount of $K_2S_2O_7$ and dissolve in cold 10% H_2SO_4. Keep the volume of the solution as small as possible. Reserve as solution (*H*).

DETERMINATION OF ZIRCONIA

The solution (*H*) is peroxidized by the addition of a distinct excess of H_2O_2 and 0.50 gram of di-ammonium phosphate added. Stir thoroughly until all the phosphate is dissolved and set aside overnight near the steam bath or oven so that, if possible, the solution will remain at about 40° C. Filter and wash with 5% NH_4NO_3. Ignite very carefully to avoid decrepitation and weigh as ZrP_2O_7. Calculate ZrO_2 equivalent and subtract from the weight of "TiO_2+ZrO_2." Calculate TiO_2%.

DETERMINATION OF MANGANESE

The solution (*E*) of a volume of about 75 ml. is warmed to 60° C., made distinctly alkaline with NH_4OH and an excess of bromine water added. It is set aside on the steam bath until the MnO_2 has flocculated. Filter through a close paper and wash a few times with water. Reserve the filtrate (*J*). Dissolve in dilute 1 : 9 HNO_3 containing a few drops of H_2O_2, boil out the excess peroxide and determine the Mn either (*a*) colorimetrically after adding 5 ml. of H_2SO_4 (sp. gr. 1.84) and 0.3 KIO_4 or (*b*) 15 ml. of $AgNO_3$ (6 grams per liter) and 10 ml. of 15% $(NH_4)_2S_2O_8$, heating to 90° to develop the permanganate color. Finish, after cooling in ice water, by adding 10 ml. of 10% NaCl and titrating with a standard sodium arsenite solution, standardized against a standard steel or against a standard permanganate.

DETERMINATION OF LIME AND MAGNESIA

The filtrate (*J*) from the MnO determination is evaporated, if necessary, to 100–120 ml., heated to boiling, and precipitated with 10 ml. of 4% ammonium oxalate solution. Let stand overnight, filter and wash with 0.5% ammonium oxalate, dissolve in dilute HCl, wash the paper several times with water, add 0.1 grams $(NH_4)_2C_2O_4 \cdot 2H_2O$ and re-precipitate boiling hot by the addition of NH_4OH. Let stand at least four hours, filter and wash as before, ignite and weigh as CaO.

The combined filtrates from the two calcium oxalate precipitations are evaporated to 200 ml. and about 1.0 gram of di-ammonium hydrogen phosphate dissolved in a few ml. of water added. Pour in 10% by volume of the solution of strong ammonia, stir vigorously while the beaker is cooled in ice water to assist precipitation, and let the magnesium ammonium phosphate stand overnight. Filter, wash with 5% NH_4OH, dissolve in hot dilute HCl, wash the paper with warm water, cool and after adding 0.1 gram $(NH_4)_2HPO_4$, re-precipitate with NH_4OH. Let stand at least 4 hours, filter, wash as before, smoke off the paper very carefully, ignite in a muffle or under good oxidizing conditions and weigh as $Mg_2P_2O_7$. Calculate to MgO by the factor .3621.

CHROMIUM, VANADIUM, AND PHOSPHORUS

The filtrate from the NaOH separation, solution (*C*), is made up to 500 ml. or 250 ml., depending on the color, and compared with a standard K_2CrO_4

solution containing approximately the same amount of sodium hydroxide. Calculate to Cr_2O_3. The amount found is generally less than .10%.

After the Cr_2O_3 determination acidify the solution and precipitate with a slight excess of NH_4OH without the use of any indicator. It will be necessary to precipitate in rather a large volume (about 1000 ml.) on account of the great amount of alumina present. Filter on one or more large loose-texture papers and wash a few times with hot 3% NH_4NO_3 to remove the bulk of the sodium salts. Transfer as much of the precipitate as possible with a platinum or porcelain spatula back to the beaker and dissolve what remains on the papers by repeatedly pouring through 100 ml. of 1 : 9 hot HNO_3. Add a few drops of H_2O_2 to the cold solution and if any color develops, compare with a standard vanadium solution colorimetrically under the same conditions. Report as V_2O_5.

After the vanadium determination transfer the solution to a 300 ml. Erlenmeyer flask, boil out the H_2O_2 and add a few drops of strong $KMnO_4$ until a pink color is present. Decolorize with a sulphite and add 15 ml. of strong HNO_3 (sp. gr. 1.42), cool, adjust the volume to about 125 ml., add 50 ml. of ammonium molybdate (Blair's formula). Shake for 10 minutes, let settle about an hour, filter on a tight paper, wash with 1% KNO_3 until free from all acid, place the paper in the flask, add an excess of standardized N/10 NaOH, shake until the paper is thoroughly disintegrated, dilute to 100 ml. with CO_2-free water, add a few drops of phenolphthalein and discharge the pink color with standard nitric acid. Bring back the pink color with N/10 NaOH and from the ratio of the acid and alkali and their respective volumes used, calculate the P_2O_5, using the ratio of 1 P_2O_5 to 46 NaOH. Standardize the NaOH against a standard sample of steel or against pure acid potassium phthalate.

Total Sulphur as SO_3.—Fuse a 2.00 gram sample with $Na_2CO_3.Na_2B_4O_7$ just as for the silica determination, using an electric muffle furnace or other means to exclude contamination by sulphur. Extract the melt with warm water, filter, and wash with 1% Na_2CO_3. Acidify the filtrate with HCl using only enough excess to give about 1% by volume. Heat to boiling and precipitate with $BaCl_2$. Let stand overnight. Filter, ignite at 900° C. and weigh as $BaSO_4$.

Soda and Potash.—A 0.5000 gram sample is pulverized to an impalpable powder by grinding in an agate motar. (On account of the abrasive action it is advisable to use an old mortar.) Determine soda and potash by the J. Lawrence Smith method. The special finger-shaped crucible is almost compulsory on account of the fact that the full heat of the Fisher burner must be used for 1.5 hrs. in order to insure complete decomposition of the sample. After the mixed NaCl and KCl are weighed, K_2O may be determined either as perchlorate or chloroplatinate. The total amount of alkali found is usually quite small, except in the case of 38 Alundum.

Blank Corrections.—One cannot emphasize too strongly the importance of applying blank corrections. These are best determined by carrying through all the steps of the analysis a pure solution of some aluminum salt known to be free from the elements sought. In the case of the Na_2O and K_2O blanks, the reagents alone are used—i.e. calcium carbonate and ammonium chloride.

Further Notes.—1. In making the colorimetric Cr_2O_3 determination one must guard against a color which may be due to the presence of platinum derived from the crucible. If Pt is suspected, acidify with HNO_3, reduce with SO_2; if the solution becomes colorless on stirring, all the color was due to Cr_2O_3. If Pt is found, match the color with M_2CrO_4 and apply the proper correction.

2. If especially accurate silica determinations are required, make double evaporations with intervening filtrations, burn off the two papers together, fuse the impure SiO_2 with one gram of Na_2CO_3 and make double evaporations with HCl (or H_2SO_4) using Pt dishes. The reason for this is that silica dehydrated from a borate solution always carries a slight contamination of B_2O_3 which is volatilized as BF_3 and counted as SiO_2.

3. Proper calcium carbonate for alkali determinations is hard to buy. It may be prepared by the precipitation of a pure calcium nitrate solution with ammonium carbonate. The $Ca(NO_3)_2$ is added hot to the ammoniacal carbonate, and the $CaCO_3$ washed about 20 times on a Buchner funnel with hot water. It is then dried at 100° C. and bottled.

4. The borax used for the fusion of the sample should be anhydrous. It may be necessary to prepare this. If the use of the deca-hydrate is attempted, the fusion is apt to froth over.

METHODS FOR THE CHEMICAL ANALYSIS OF ALUMINUM AND ALUMINUM ALLOYS [22]

SAMPLING

Securing representative samples is of paramount importance for satisfactory chemical analysis. Chemists, at best, work on samples weighing a few grams each. These samples may represent many thousands of pounds of metal or other material. Unless, for example, sampling procedures are designed in the light of a full knowledge of the structure of metals, and the behavior of metals during solidification from a molten condition, the sample secured is not apt to be representative.

It is obvious that the sampling of aluminum is best done when the metal is molten. From the molten metal, which has been brought to a uniform composition by thorough mixing, a ladle of metal is withdrawn and a sample coupon is poured in the form of a flat plate in a steel mold. This plate is $1\frac{7}{8} \times 3 \times \frac{3}{16}$ inches. The actual material for analysis is taken by repeated drilling in a diagonal line across the plate. Commercially pure aluminum, as tapped from

[22] Churchill, H. V., and Bridges, R. W., "Chemical Analysis of Aluminum" (1935).

a reduction furnace, is sampled by pouring into a button mold. This mold is about 2 inches in diameter and 1½ inches deep. This button is drilled completely through from top to bottom.

In all sampling work, cleanliness is essential. The use of oil should be avoided in drilling, wherever possible. Pick-up of iron should be avoided by the use of sharp drills. It is a wise precaution to treat prepared samples with a magnet to remove adventitious iron.

Notch bar and ingot sampling is somewhat more difficult than is the sampling of molten metal. In the case of notch bar, at least four notches should be drilled, preferably completely through the ingot. In the case of ingots, at least six drillings should be made, which extend at least half way through the ingot. Three of the drillings should be made on the top of the ingot and three on the bottom. The three drillings on each side should be in a line from one corner of the ingot to the diagonally opposite corner. Such samples are to be thoroughly mixed, observing the above mentioned precautions as to cleanliness.

Where rich alloys are being handled, which are brittle, crushing should be used instead of drilling. The resultant sample is ground to completely pass a 40-mesh sieve, and, as usual, a magnet should be used on the product.

The sampling of sheet, castings, or fabricated forms of the metal, is not specially difficult. However, particularly in the case of castings, it is possible that an accurate sample can be secured only by drilling in a number of separated locations and carefully compositing all the drillings obtained. In the case of sheet, there is no hazard in taking chippings or drillings at random until a sufficient quantity of sample is obtained. Sampling of other fabricated forms of aluminum should be done with the thought in mind of avoiding in so far as is possible, segregation of some constituent in the alloy.

The sampling of scrap or such material is very difficult to do in a satisfactory manner. It is a basic fact that such materials are best sampled by melting the material, thoroughly mixing, and then sampling the resultant molten metal.

The value of any analysis depends upon the skillful application of adequate chemical procedures to a representative sample. Chemists called upon to make analyses should always know the purpose of such analyses, so that they may have a criterion for evaluating the sampling procedures employed.

The direct determination of aluminum in aluminum and aluminum alloys is tedious and difficult and is not made in commercial work. The percentage of aluminum, if required, is assumed to be the remainder after the sum of the determinable elements is subtracted from 100%.

Elements quite often present in determinable amounts in aluminum and aluminum alloys are Silicon, Iron, Copper, Titanium, Nickel, Lead, Zinc, Magnesium, Manganese, Chromium, and Tin. Methods for the determination of these elements will be given in the following procedures.

When a large number of elements are present in an alloy it is often convenient to determine several of them on the same sample weight. For example, it is feasible to determine Silicon, Iron, Copper, Titanium and Nickel on a single 1 g. weight and Lead, Copper, and Zinc on a single 2 g. weight of sample. The other elements mentioned above are each usually determined on separate weights of sample.

Detailed procedures for the determination of these elements are as follows:

DETERMINATION OF SILICON

Place 1 g. of sample in a medium-sized casserole or beaker (or 0.5 g. if a silicon content higher than 10% is expected). Keeping the vessel covered as much as possible, cautiously add 35 ml. (or 20 ml. for a 0.5 g. sample) of acid mixture No. 1, p. 29. The action is violent with high silicon alloys. When no further action can be seen, evaporate till heavy fumes of sulfuric acid are evolved for a few minutes. Cool, moisten with 10 ml. of 1 : 3 sulfuric acid, add 100 ml. of hot water, and boil till salts are dissolved. Stir in some paper pulp, filter through a close-textured paper, then wash three or four times with hot water. (Reserve filtrate for copper determination.)

Ignite the residues in a large platinum crucible. After cooling, mix with them 1 to 8 g. (depending on the amount of residue) of sodium carbonate. Fuse cautiously till nearly quiet, then finish with a strong heat. Run the melt up the sides of the crucible, cool, and place in a casserole or beaker with sufficient 1-3 sulfuric acid to prevent formation of solid cake of sodium sulfate when taken to fumes. When the melt has dissolved, remove the crucible, washing it out into the vessel. Evaporate and continue heating till heavy fuming has taken place for some time, then remove from heat. While still moderately warm, add a little cold water followed by 100 ml. of hot water. Heat to complete solution of the soluble salts, but avoid too long treatment as the silica tends to redissolve. Filter after stirring in some paper pulp, and wash thoroughly with hot water.

Dry the filter with contents, then ignite in a platinum crucible at 500° C. until free from carbon, finish at 1000° C., cool, and weigh. Moisten with a few drops of diluted sulfuric acid and add several ml. of hydrofluoric acid. Evaporate dry, ignite, cool, and weigh again. The loss in weight represents silica. Deduct a determined blank.

Silicon = silica × 0.4672.

Note 1.—In routine analysis, fusion of the first residue may be omitted if it contains no elemental silicon, indicated by white color. In this case, the residue may be treated with H_2SO_4 and HF, and the loss in weight calculated to silicon. The slight loss of silica in the filtrate may be ignored. For accurate work, however, silica must be recovered from the filtrate by a second dehydration.

Note 2.—If an aluminum alloy containing silicon and magnesium, combined as silicide; or containing silicon in solid solution (maximum solid solubility of silicon in aluminum is about 1.5%, obtained by annealing at 570° C. and quenching in cold water) is dissolved in acids, some loss of silicon may occur. Hence, for the determination of silicon in an alloy of this kind or for fundamental umpire analysis wherein the thermal history is unknown, an " Alkali Attack " method such as the following should be used.

Sodium Hydroxide Solution Method

Dissolve 0.5 to 1.0 gram of sample in a covered Monel metal beaker, using 15 ml. of 30% sodium hydroxide solution. When violent action ceases, place on a hot plate and heat gently until the volume of solution is reduced to about 5 ml. If the solution is still dark, add 2 or 3 ml. of 3% hydrogen peroxide to hasten oxidation and again reduce the volume to about 5 ml. Transfer the concentrated sodium hydroxide solution to a Pyrex beaker containing 80 ml. of 1 to 1 sulfuric acid. Thoroughly police the Monel metal beaker and, using a few cubic centimeters of dilute sulfuric acid, wash any adhering material into the Pyrex beaker. Add 2 ml. of concentrated nitric acid. Evaporate to copious fumes and finish by the usual silica volatilization procedure.

Alternative Method. (This procedure is now preferred to the one given above because after dehydration salts are more easily dissolved.) Transfer the solution to a

Pyrex beaker containing 65 ml. of 1 to 1 sulfuric acid and 20 ml. of 60% perchloric acid. Thoroughly police the Monel beaker and cover and, using a few cubic centimeters of dilute sulfuric acid, wash any adhering material into the Pyrex beaker. Make double dehydration by evaporation to copious fumes and finish by usual silica volatilization procedure.

Another alternative procedure, substantially as published by the Aluminum Research Institute, is: Neutralize the concentrated sodium hydroxide solution with 1 to 1 hydrochloric acid and transfer it to a Pyrex beaker. Add 20 ml. of 60% perchloric acid. Evaporate to copious fumes, cool, add 50 ml. of hot water, bring to a boil, filter at once using an ashless paper pulp, and wash with warm 1% hydrochloric acid. Add 10 ml. of perchloric acid to filtrate, fume, and filter as before. Dry the filters with contents, then ignite in a platinum crucible at 1000° C. Add a few drops of sulfuric acid and ignite to constant weight. Cool and weigh. Finish by the usual silica volatilization procedure.

DETERMINATION OF COPPER

Iodide Copper

Pass a rapid stream of hydrogen sulfide through the silicon filtrate for 5 minutes or add 50 ml. cold saturated hydrogen sulfide solution. Heat just to boiling to coagulate the sulfide, filter, and wash with acidulated hydrogen sulfide water. (Reserve filtrate for determination of iron.)

Ignite the precipitate at 500° C. in a porcelain crucible, cool, dissolve in 5 ml. nitric acid, transfer to a beaker or flask containing 0.2 to 0.5 ml. sulfuric acid. The amount is determined by the size of the sulfide residue. Transfer the vessel to the hot plate and take to dryness, using care to avoid spattering. Continue heating till no more sulfuric anhydride fumes from free acid come off. This heating must not be so strong that it decomposes the sulfates, turning the residue brown. After cooling, add 25 ml. of water containing 3 ml. of 99.5% acetic acid. Heat to complete solution, but avoid boiling off much of the liquid. Remove the vessel from the hot plate. To the cooled solution add 5 ml. of potassium iodide solution (30 g. potassium iodide to 100 ml. of water), or 10 ml. if the copper is over 1%, and shake thoroughly. Allow to stand 5 minutes (10 minutes with the larger addition). Titrate the free iodine with a solution of sodium thiosulfate having a suitable copper value standardized by the Copper Sulfate Method. A few drops of fresh starch solution (1 g. of soluble starch to 150 ml. of water) used as an indicator, are added near the end of the titration.

Note.—At the stage of driving off the free acids, the upper part of the container can be freed from acid readily, without overheating the bottom, by surrounding the group of containers with shields.

Preparation and Standardization of Thiosulfate Solution by Copper Sulfate Method.—Using distilled water, prepare a solution of appropriate strength by dissolving the pure crystals of sodium thiosulfate in one of the following ratios, dependent upon the copper value desired:

16 g. per liter: 1 ml. = 0.004 g. copper approximately.

4 g. per liter: 1 ml. = 0.001 g. copper approximately.

2 g. per liter: 1 ml. = 0.0005 g. copper approximately.

Weight 15.9 g. of C.P. copper sulfate pentahydrate and dissolve in distilled water to a total volume of 2 liters, including 5 ml. of glacial acetic acid to prevent hydrolysis. This solution will contain about 0.002 g. of copper per ml.

Accurately determine the copper value per ml. by electrolyzing three separate 50 ml. portions measured with a 50 ml. pipette.

To standardize the strong thiosulfate solution, pipette 50 ml. of the copper sulfate solution into a 250 ml. Erlenmeyer flask, add 3 ml. 99.5% acetic acid and 10 ml. potassium iodide solution (30 g. potassium iodide to 100 ml. water). After mixing and allowing to stand 10 minutes, titrate it with the sodium thiosulfate solution to be standardized. A few drops of fresh starch solution (1 g. soluble starch dissolved in 150 ml. water) are added near the end of the titration.

The weak thiosulfate solutions are standardized in the same way except that only 10 ml. of the copper solution is used, 15 ml. water added, and 5 ml. potassium iodide solution taken instead of 10 ml.

The copper content of the standard copper sulfate solution used, divided by the number of ml. of thiosulfate solution required, will equal the copper value of 1 ml. of the sodium thiosulfate solution.

A thiosulfate solution sometimes loses strength at an appreciable rate, the quality of crystals or water, or the condition of storage appearing to influence the keeping quality. It is advisable to standardize for each day's use unless proof is obtained that a longer interval can be safely allowed.

DETERMINATION OF COPPER

Electrolytic Method.—A nitric acid solution of the ignited residue obtained from the " Formic acid Hydrogen sulfide precipitate " in the determination of lead, or from the " Hydrogen sulfide precipitate " from silicon filtrate may be used for the electrolytic determination of copper.

A method using caustic solution of sample is as follows.

Place 1 g. sample in a 250 ml. Erlenmeyer wide mouth flask or beaker.

Add 15 ml. of 20% sodium hydroxide solution. When reaction subsides, heat until solution is complete, dilute with 100 ml. hot boiled distilled water. filter, and wash with hot water. Using hot 1 : 1 nitric acid, completely dissolve the residue into a beaker for electrolysis. Neutralize with 1 : 1 ammonia, make acid with 1 : 1 sulfuric acid, and add 4 ml. excess. Add 1 ml. of concentrated nitric acid. Dilute to 150 ml. Using any convenient stirring device, electrolyze until copper is completely deposited. In case no stirring device is available, the copper can be plated out by lowering the current density sufficiently to give a pure weighable deposit, and allowing a longer time.

Remove the cathode, wash with water and alcohol, dry at 100° C., cool to room temperature, and weigh. The gain in weight represents copper.

NOTE.—Small amounts of iron, aluminum, cobalt, nickel, and manganese do not affect the electrolytic determination of copper as outlined above. However, if the amount of metals other than copper is large, it is best to make a hydrogen sulfide separation by the following procedure: Using a minimum amount of hot 1 : 1 nitric acid, completely dissolve the residue obtained from the sodium hydroxide solution. Avoid an excess of nitric acid at this point as later it will decompose hydrogen sulfide, precipitating free sulfur. Make the solution alkaline with ammonium hydroxide and then just acid with hydrochloric acid. Dilute to 150 ml. with water. Saturate the solution with hydrogen sulfide, filter, and wash free from acid. Ignite the precipitate at 500° C. in a porcelain crucible, cool, dissolve in 5 ml. of nitric acid, using gentle heat, neutralize with 1 : 1 ammonium hydroxide and complete as in the main method. A similar procedure may be followed using the silicon filtrate.

DETERMINATION OF IRON

Use the filtrate from the copper sulfide filtration (determination of copper). Place it in a wide mouth Erlenmeyer flask on a hot plate. Add 4 or 5 solid glass beads having a diameter of about 5 or 6 mm., to prevent bumping, and boil vigorously to remove hydrogen sulfide. It will be driven off in 25 to 30 minutes. As soon as the hydrogen sulfide is expelled, cool the flask. When the solution is cold, titrate the iron with standard potassium permanganate having an iron value of 0.001 g. per ml. Deduct a blank which is determined by a titration made on a solution obtained by carrying along with the regular determination a flask to which all reagents used have been added.

NOTES.—1. Vanadium is the only element likely to be present in aluminum which will interfere with the iron determination. Usually it is present in such small amount that it can be ignored. An accurate method which eliminates the interference of vanadium is as follows. Dissolve 1 g. of sample in an acid mixture as for determining silicon and continue till the first residue has been ignited. Volatilize the silica and silicon by heating with a little hydrofluoric, nitric, and sulfuric acids, evaporate to fumes, and add to the original filtrate. Stir in 25 ml. of 25% tartaric acid solution. Pass in hydrogen sulfide and filter off the precipitate, washing with acidulated hydrogen sulfide water. (0.1% solution of sulfuric acid saturated with hydrogen sulfide.) Add ammonium hydroxide to the filtrate in small excess. Treat with hydrogen sulfide for one minute, warm to coagulate the precipitated sulfide, then cool, filter, and wash with a solution containing 1% each of ammonium sulfide and ammonium sulfate. Dissolve the sulfide from the filter with 40 ml. of warm 1 : 6 sulfuric acid, washing the paper thoroughly with hot water. Boil out hydrogen sulfide and finish by procedure given above.

2. The success of the iron determination depends largely on the temperature of the hot plate used to expel the hydrogen sulfide. It is essential that the solution boil vigorously.

3. The stability of the reduced iron in the solution has been thoroughly investigated. It was found that, after a 2½ hour exposure to the atmosphere, samples containing up to 12% iron showed a negligible oxidation of ferrous iron.

4. Potassium thiocyanate may be used to test complete reduction of iron. This should be done by removing a drop of solution and testing on a spot plate.

5. Lead acetate paper may be used to test for complete removal of hydrogen sulfide. However, it will be safe to omit the test if the samples are boiled 30 minutes.

6. In all work it is very desirable that the volume of the solution be kept as low as possible. This aids the removal of the hydrogen sulfide from the solution containing the ferrous iron and is required if titanium is determined, as the volume must be low enough for a 100 ml. Nessler tube to hold it.

DETERMINATION OF TITANIUM

Transfer the solution in the flask, after the iron has been titrated, to a 100 ml. Nessler tube. In a duplicate tube place 20 ml. of 1 : 3 sulfuric acid and 75 ml. of water. The sample is apt to have a faint yellow tinge and the standard is made to match by adding the required amount of strong ferric solution (1.8 g. of ferric sulfate and a little sulfuric acid to 100 ml. of water).

Add 3 ml. of 3% hydrogen peroxide to each tube and mix the contents of each. Add sufficient standard titanium solution (1 ml. = 0.0001 g. titanium) to the second tube to match the color of the sample.

The titanium may be measured by comparison with previously prepared standards or a colorimeter may be used.

NOTE.—For preparation of standard titanium solution see p. 30.

DETERMINATION OF NICKEL

The filtrate from the silicon determination may be used for the determination of nickel. If copper has been removed with H_2S, the H_2S must be boiled out and the solution oxidized by adding 3 ml. of concentrated nitric acid and boiling. If iron and titanium have been titrated, 3 ml. of nitric acid should be added and the solution boiled vigorously for a few minutes. Hydrogen peroxide must be removed. Dilute the solution to 200 ml.

Add 25 ml. of 25% tartaric acid and neutralize with ammonia. If there is insoluble material at this point filter. Heat nearly to boiling and stir in dimethylglyoxime solution (1 g. in 100 ml. concentrated ammonia), using 20 ml. for up to 0.02 g. of nickel and 5 ml. for each additional 0.01 g. If nickel content is over 0.25%, filter through a weighed Gooch crucible 30 minutes after precipitating; if less than 0.25% allow to stand 1 hour before filtering. Wash with hot water, dry for 2 hours at 110 to 120° C., cool and weigh.

Nickel = nickel dimethylglyoxime $\times$ 0.2032.

NOTES.—1. If much cobalt is present precipitate as usual, make just acid with acetic acid and add 3 ml. of dimethylglyoxime. Allow to stand for 1 hour, filter on hardened paper, wash with hot water, dissolve with cold 1 : 3 hydrochloric acid, neutralize with ammonium hydroxide, and add 10 ml. dimethylglyoxime.

2. Nickel may be determined in the residue after dissolving the aluminum in 20% sodium hydroxide solution. Dissolve the residue in HCl and a little HNO_3. Add H_2SO_4 and fume to dehydrate silica. Treat the solution of soluble salts with H_2S and remove silica and copper sulfide together. Finish by procedure given above.

DETERMINATION OF LEAD

Electrolytic Method.—Dissolve a 2 g. sample in a 250 ml. flask in 60 ml. of 1 : 1 hydrochloric acid, added cautiously, followed by 1 ml. of concentrated nitric acid toward the end of the reaction. Boil to complete the solution and to expel the oxides of nitrogen. Dilute to about 125 ml. volume and filter into a 400 ml. beaker, washing with hot water. To the filtrate add 50 ml. of 25% tartaric acid solution, dilute to 300 ml. and neutralize with ammonium hydroxide using methyl red as an indicator, then add 25 ml. of a formic acid mixture made by diluting 200 ml. of formic acid (sp. gr. 1.20) to 970 ml. and adding 30 ml. of concentrated ammonium hydroxide. Heat nearly to boiling and pass in a rapid stream of hydrogen sulfide for 15 minutes. Stir in a little macerated paper and heat to aid coagulation of the precipitate. Set a moderately close paper with a solution made by diluting 25 ml. of the above formic acid mixture to 1 liter and saturating with hydrogen sulfide, filter and wash 8 times with the same solution. Ignite the precipitate in a porcelain crucible at 500° C. Transfer ignited residue to a 200 ml. tall form beaker and dissolve in 5 ml. concentrated nitric acid. If tin is present evaporate to small volume, filter off the stannic acid and thoroughly wash with dilute nitric acid and then hot water. Adjust the volume of the solution or filtrate if the tin separation is made to 150 ml., and electrolyze hot, using a low current density. After electrolysis is complete, remove the anode, washing first with water and then with alcohol, dry at 125° C., cool and weigh.

Lead = lead dioxide $\times$ 0.8643 (empirical).

NOTES.—1. Copper may be determined from its weight on the cathode where it can be deposited when lead is determined.

2. The electrolyte may be used for determination of zinc. See Note 2, Oxide Method.

DETERMINATION OF ZINC

Zinc Oxide Method.—Use 1 g. sample if zinc content is above 1%, 2 g. sample if zinc content is 0.10 to 1.0% and 3–5 g. sample if zinc is below 0.10%; electrolyte from determination of lead may be used for determination of zinc (Note 2).

Dissolve the sample in a covered 400 ml. beaker in 1 : 1 hydrochloric acid, added cautiously, followed by 1 ml. of nitric acid toward the end of the reaction. For 2 g., use 40 ml. of acid; for 1 g. 25 ml. Boil to complete the solution and to expel oxides of nitrogen. Dilute to 125 ml., add 10 ml. 1 : 1 hydrochloric acid, pass hydrogen sulfide through the solution for 3 minutes, add a little macerated paper, filter, and wash with acidulated hydrogen sulfide water. Boil the filtrate 10 minutes to expel hydrogen sulfide. Cool somewhat, add 25 ml. of 25% tartaric acid per gram of sample, dilute to 250 ml., neutralize with ammonium hydroxide, using methyl red indicator, then add 25 ml. of a formic acid mixture made by diluting 200 ml. of formic acid (sp. gr. 1.20) to 970 ml. and adding 30 ml. of concentrated ammonium hydroxide. Heat nearly to boiling and pass in a rapid stream of hydrogen sulfide for 15 minutes. Stir in a little macerated paper and heat to aid coagulation of the precipitate. Set a moderately close paper, containing a little macerated paper, with a solution made by diluting 25 ml. of the above formic acid mixture to 1 liter and saturating with hydrogen sulfide, filter, and wash 5 times with the same solution. Dissolve the zinc sulfide from the filter into the original beaker with hot 1 : 3 hydrochloric acid, and wash the paper thoroughly. Boil for 5 minutes. Cool somewhat, add 5 ml. of 25% tartaric acid, and make the solution just alkaline to methyl red with ammonium hydroxide. Dilute to 100 ml., heat, and pass hydrogen sulfide through the solution for 3 minutes. Add 10 ml. of the formic acid mixture and continue the hydrogen sulfide for 5 minutes more. Coagulate and filter as above, and wash 5 times with the formic acid wash solution. Ignite the precipitate in a weighed porcelain or vitreosil crucible, starting at a dull red heat and finishing at a moderate red. Cool and weigh as zinc oxide. Deduct a determined blank.

Zinc = zinc oxide $\times$ 0.8034.

NOTES.—1. A dark zinc sulfide precipitate indicates the presence of lead, and the weighed precipitate should be examined and corrected. Dissolve the oxide in nitric acid and determine lead by the electrolytic method. Correct the weight of zinc oxide for the amount of lead sulfate present.

2. If an appreciable amount of lead is present, necessitating its determination, as is generally the case in the analysis of secondary aluminum, it is most convenient to determine zinc in the electrolyte after the determination of lead. The procedure is as follows: Add 5 ml. of concentrated sulfuric acid to the electrolyte, and evaporate to fumes of sulfuric acid. Take up with water, add 25 ml. of hydrogen sulfide water, bring to a boil, filter, and wash thoroughly. Finish by the oxide or the mercury thiocyanate method.

3. When it is necessary to use a large sample it may conveniently be divided into several portions for the first sulfide precipitation, the precipitates dissolved into a single beaker, and the procedure continued as in the standard method.

4. If cobalt is present, make the first precipitation, filter, and dissolve in hydrochloric acid as in the standard method. Evaporate to small volume, dilute, and add sodium hydroxide in excess, followed by sodium peroxide, allow to stand, filter, make the filtrate just acid with hydrochloric acid, add 5 ml. of 25% tartaric acid, and continue as in standard method.

DETERMINATION OF ZINC

Mercury Thiocyanate Method.—(The solution from determination of lead can be used for determination of zinc. See Note 2, Oxide Method.)

Place 1 g. of drillings in a 250 ml. beaker or Erlenmeyer wide mouth flask. Dissolve in 35 ml. of acid mixture No. 1. When completely dissolved, evaporate till heavy fumes of sulfuric acid have been evolved for a few minutes. Cool somewhat, add 10 ml. of 1 : 3 sulfuric acid followed by 60 ml. of hot water, and boil till the salts are dissolved. Add 50 ml. of a cold saturated aqueous solution of hydrogen sulfide and remove from the hot plate as soon as the solution begins to boil. To the filter paper, set in the funnel, add some paper pulp, filter off the silica and copper sulfide, and wash 4 times with hot water. Receive the filtrate in a 400 ml. beaker. Place the beaker on a hot plate and boil vigorously to remove hydrogen sulfide. As soon as the hydrogen sulfide is expelled, remove the beaker from the hot plate and cool to room temperature. Oxidize the iron with permanganate. Add 5 ml. hydrochloric acid, dilute to 150 ml. and, while stirring the solution vigorously, add 25 ml. of ammonium mercuric thiocyanate solution, (note 1) and allow to stand overnight. Frequent stirring will hasten complete precipitation. Collect the precipitate on a weighed Gooch crucible, wash with a solution containing 10 ml. of the precipitating reagent per liter, dry at 105° C., cool, and weigh. Deduct a determined blank.

Zinc = zinc mercuric thiocyanate × 0.1289 (empirical).

NOTES.—1. Mercuric Ammonium Thiocyanate Reagent: Dissolve 32 g. of ammonium thiocyanate and 27 g. mercuric chloride in 500 ml. water. Filter off any residue.

2. For samples containing over 1% nickel or low amounts of zinc, make the standard formic acid-sulfide separation. Follow method 30-A till the first hydrochloric acid solution of the zinc sulfide precipitate is obtained. Add 10 ml. of 1 : 1 sulfuric acid to the filtrate and evaporate to fumes. Dilute to 100 ml., filter, and wash. Continue with the ammonium mercuric thiocyanate precipitation as outlined in the above method. This separation, which removes aluminum as well as nickel, will greatly reduce the time required (from overnight to about 2 hours) for complete precipitation of the zinc.

DETERMINATION OF MAGNESIUM

Pyrophosphate Method.—Weight of Sample: For magnesium contents up to 1 or 2 tenths of a per cent, use 2 g., for higher magnesium contents use 1 g. or less. Dissolve the sample using 15 ml. of 20% sodium hydroxide solution per g. For solution of alloys high in silicon a second treatment with caustic is necessary. (See Note 2.) When solution is complete, judging by the evolution of hydrogen, filter through paper of close texture and wash 5 times with hot 1% sodium carbonate solution. Dissolve the residue from the filter with a few drops of nitric acid and 40 ml. of hot 1 : 1 hydrochloric acid, receiving it in the original container, and wash the filter with hot water. Neutralize this solution with ammonium hydroxide, and add a few drops excess. Add 5 ml.

of a fresh solution of ammonium sulfide (800 ml. water and 200 ml. of ammonium hydroxide, saturated with hydrogen sulfide). Filter into a 250 ml. beaker and wash a few times with a liquid prepared by adding 10 ml. of concentrated ammonium hydroxide and 10 g. of ammonium chloride to 500 ml. of water and saturating with hydrogen sulfide. Boil the filtrate vigorously to drive off the ammonium sulfide. The volume of the solution should be held at about 75 ml. at this stage by adding distilled water to replace that lost by evaporation. Oxidize the finely divided precipitated sulfur by adding 10 ml. of bromine water and continue boiling until the color of bromine is gone. Again add 10 ml. of bromine water and while stirring vigorously make the solution alkaline with ammonium hydroxide and add 10 drops excess. Digest until the MnO_2 flocks out. Filter and wash 5 times with hot water. Make the filtrate acid with hydrochloric acid, add 10 drops excess, and boil till the bromine is gone. Add 2 drops of 0.1% methyl red indicator. Complete removal of bromine is indicated when the indicator holds its color without fading. Add ammonium hydroxide until the color changes to distinct yellow and then add a few drops excess. Add 10 ml. of saturated ammonium oxalate solution, digest near the boiling temperature for one hour, keeping ammoniacal. Filter through a small, close-textured paper and wash 8 times with small portions of hot water. The calcium content of aluminum and aluminum alloys is normally too low to interfere with the magnesium determination, so that the procedure for its removal may be omitted unless calcium has been added. Make the filtrate just acid with hydrochloric acid and adjust the volume to 125 ml. Add 10 ml. of 10% diammonium phosphate solution, and cool. Add 15 ml. of ammonium hydroxide and stir vigorously till the precipitate begins to form. Allow to stand for at least one hour. Filter and wash with a cold solution prepared by mixing 900 ml. of water, 40 ml. of nitric acid and 100 ml. of ammonium hydroxide. Place in a weighed porcelain or vitreosil crucible, dry and ignite till completely white. Weigh as magnesium pyrophosphate and deduct a blank.

Magnesium = magnesium pyrophosphate $\times$ 0.2184.

NOTES.—1. If more than 2% of magnesium is present, some of it may be carried down with the sulfides. In that case, dissolve the precipitate with 10 ml. of 1 : 1 hydrochloric acid, neutralize, and add a few drops of ammonium hydroxide, precipitate and filter off the sulfides as before, then combine the filtrates.

2. A complication arises when samples high in silicon are treated by the procedure just mentioned. In this case a large part of the silicon is dissolved in an oxidized state, and a precipitate, presumably of aluminum silicate, settles out, which is difficult to handle in the subsequent operations. If the attack is made first with weak alkali, the aluminum will dissolve fairly completely, without much attack on the silicon and is removed by filtration. Subsequent addition of very strong alkali to the residue will remove the silicon without precipitation of silicates. A convenient method for solution of 2 g. is as follows: Place sample in 250 ml. beaker, add 175 ml. cold water, place the beaker in a water cooling tray. Add 25 ml. of cold 50% sodium hydroxide solution. The speed of addition must be controlled according to the fineness of sample. Let stand until hydrogen evolution ceases. Filter through paper of close texture and wash 5 times with hot 1% sodium carbonate solution. Wash the undissolved residue from the paper back into the original beaker, add 5 g. solid sodium hydroxide and 50 ml. water and digest until the silica is dissolved. Dilute to 200 ml. and filter on the original paper. Wash the final insoluble residue and continue by usual procedure. When much silicon and much magnesium occur in the same alloy, the resulting magnesium silicide, recognizable by its dark blue color, remains unaffected by the alkali; it is neces-

sary to decompose it with acid and dehydrate the silica before proceeding further. This combination is of rare occurrence.

3. For the determination of small amounts of magnesium in aluminum alloys or scrap metal, containing a number of heavy metals, it is convenient to make a mercury cathode separation by means of Melaven's electrolytic cell. Fig. 2.

Procedure.—Follow method for determination of Mg. until solution of residue containing calcium, magnesium, etc., is obtained. Add 10 ml. of concentrated sulfuric acid and evaporate to copious fumes. Cool, dilute to 100 ml. with hot water. Boil until salts are in solution, allow to settle and filter with a little paper pulp. Wash well with hot water. To the filtrate add ammonium hydroxide until a slight permanent precipitate forms; warm and add 1 : 1 sulfuric acid dropwise till the precipitate redissolves. Make up to 200 ml. and electrolyze. When electrolysis is complete, withdraw the electrolyte, add 10 ml. of concentrated hydrochloric acid and make a double ammonium hydroxide separation. Adjust the filtrate to a volume of about 75 ml. Make the bromine separation, oxalate precipitation of calcium, and determine magnesium by the usual procedure.

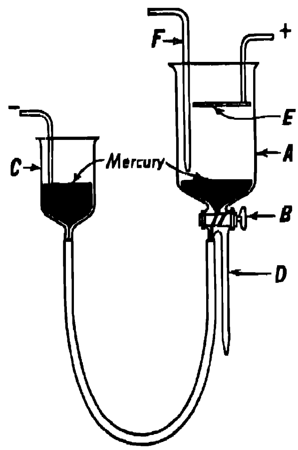


FIG. 2.—Mercury Cathode (Melvan Cell).

A. Cylindrical glass vessel with conical base.
B. Two-way stop cock.
C. Leveling bulb.
D. Glass tube constructed in same manner as a burette tip.
E. Platinum anode.
F. Glass tube for introduction of air to stir electrolyte.

8-hydroxyquinoline method.—Follow the pyrophosphate method until the acid filtrate is obtained in a 250-ml. wide mouth Erlenmeyer flask and diluted to 150 ml. Add a 5% alcoholic solution of 8-hydroxyquinoline (5% 8-hydroxyquinoline in 95% methyl or ethyl alcohol) in excess, which is indicated when the supernatant liquid is yellow after the precipitate has settled. Five ml. is sufficient to precipitate 15 milligrams of magnesium. Neutralize the solution with ammonium hydroxide and add 5 ml. excess. Heat the solution just to boiling, remove it from the source of heat, and allow to stand 15 to 20 minutes. Filter and wash free from ammonia with cold water. Finish by one of the following procedures, *A* or *B*.

Procedure A (Bromate Iodide Method) (preferred procedure).—Dissolve the magnesium oxinate into the flask in which it was precipitated, using 30 ml. of hot 1–1 hydrochloric acid, and wash thoroughly with cold water. Dilute the filtrate to 150 ml. with cold water. Add bromate solution (2 g. potassium hydroxide, 80 g. potassium bromide and 9.156 g. potassium bromate dissolved in 1000 ml. water) from a burette (1 ml. = 0.001 g. Mg.) in excess. This can be estimated by use of one drop of methyl red. Bromate is added until methyl red fades and then add 2 or 3 ml. more. Immediately add 10 ml. of 30% potassium iodide and titrate with thiosulfate (1 ml. = 0.001 g. Mg.).

$$\frac{\text{ml. of Bromate} - \text{ml. of Thiosulfate} \times 100}{\text{Wt. of Sample}} = \%\ \text{Magnesium}$$

Procedure B (Sulfuric Acid Titration).—Place the magnesium oxinate precipitate with the paper in the flask in which it was precipitated. Add 0.1 N sulfuric acid in amount about double that required to react with the magnesium

oxinate (10 to 20 ml.). Stopper the flask and shake violently until the magnesium oxinate is dissolved, add 10 ml. of phenol red indicator (0.5 g. phenol red dissolved in 125 ml. methyl alcohol and diluted to 1000 ml. with water), and 50 ml. of ethyl ether and again shake. Titrate with 0.1 N sodium hydroxide to red and again shake (red will probably fade) and titrate to red again. If over-titrated, back titrate with acid and finish with sodium hydroxide to the phenol red end point.

$$\frac{\text{ml. 0.1 N Sulfuric acid} - \text{ml. 0.1 N Sodium hydroxide} \times 0.001216 \times 100}{\text{Wt. of Sample}} = \%\ \text{Magnesium}$$

DETERMINATION OF MANGANESE

Place a 0.2 g. sample in a 250 ml. Erlenmeyer wide mouth flask. Add 20 ml. of acid mixture No. 2. Place upon a hot plate and heat until solution is complete. Remove the flask from the source of heat, cool, add 10 ml. of silver nitrate solution (3 g. per liter) and 90 ml. of hot water containing 1 g. of ammonium persulfate. Heat gently until the permanganic acid is fully developed and cool to room temperature.

At this stage samples having a manganese content of 0.03% or less are determined colorimetrically. This is done by comparing the samples with standard solutions having a manganese value of 0.00, 0.01, 0.02 and 0.03%.

Titrate the samples having higher manganese content with a standard solution of sodium arsenite, 1 ml. having a value of 0.0002 g. manganese.

Standard Solution.—Dilute the required amount of stock solution, p. 31 (about 65 ml.) to 1000 ml. After 24 hours, standardize this solution by using it to titrate the manganese contained in a standard aluminum-manganese alloy.

NOTES.—1. After the sample has been decomposed there may remain some unoxidized silicon which would interfere with the titration because of the color it would give the solution. Such silicon may be removed by adding a few drops of hydrofluoric acid, while nitric acid is still present.

2. The precipitation of silver chloride by the addition of 2 ml. of sodium chloride solution (2 g. of sodium chloride to 1 liter of water) will give an end point more easily observed.

3. The analytical procedure used on samples must be an exact duplication of that employed on standardizing the sodium arsenite solution.

4. The standards for colorimetric comparison are prepared by carrying flasks, to which all reagents are added, along with the samples. To these add a standard solution of potassium permanganate having a value of 0.001 g. iron or 0.000197 g. manganese per ml. till the known value of manganese desired is reached.

DETERMINATION OF CHROMIUM

Reagents.—No. 2 acid. See p. 29. Silver nitrate solution. 3 g. silver nitrate dissolved in 1 liter of water. Ammonium persulfate crystals. Standard potassium permanganate 0.1 to 0.05 N. Standard ferrous ammonium sulfate of same strength.

Procedure.—Place 1 g. of sample in a 400 ml. beaker, add 30 ml. of No. 2 acid, 20 ml. silver nitrate solution, and heat gently until sample is dissolved. Boil to expel the oxides of nitrogen. Dilute to 300 ml. with hot water, add

2 g. of ammonium persulfate and bring to a boil. *A*. If no manganese is present, boil for 20 minutes, cool, run in standard ferrous ammonium sulfate and titrate back with standard permanganate. *B*. If manganese is present up to 0.10%, boil for 10 minutes, add 2 ml. of 1 : 1 hydrochloric acid and boil for an additional 10 minutes, cool, and titrate as above. *C*. If manganese is over 0.10%, boil for 3 minutes, add 2 ml. of 1 : 1 hydrochloric acid and continue boiling for 20 minutes. Cool and titrate.

Iron value of ferrous ammonium sulfate minus iron value of potassium permanganate times 0.3105 equals chromium.

DETERMINATION OF TIN

A 500 ml. Erlenmeyer flask is used, provided with a 1-hole stopper carrying a glass tube bent so that the outer portion, several inches long, will project downward when in position. Place 1 to 3 g. of sample in the flask, with .25 g. of pure powdered antimony. Add 100 ml. of 1 : 1 hydrochloric acid, insert the stopper and arrange so that the outer end of the tube dips into a vessel of saturated sodium bicarbonate solution. After the reaction slackens, heat the flask, finally boiling for about 10 minutes to insure complete solution of the tin. Cool the flask gradually with the tube still dipping in the sodium bicarbonate solution. The latter will be drawn in as the flask cools, supplying carbon dioxide to prevent entrance of air. As soon as cold, open the flask and, without delay, add 0.5 g. potassium iodide, 2 or 3 ml. of fresh starch solution (1 g. starch to 150 ml. water), then titrate to a blue color with standard potassium iodate solution. Deduct a determined blank.

Iodate Solution.—Dissolve 1.8 g. of potassium iodate, 20 g. of potassium iodide and 2 g. of potassium hydroxide in water and dilute to 1 liter. To standardize it, use a solution containing a known amount of pure tin dissolved in hydrochloric acid. Place a measured portion of the tin solution in a flask with 1 g. of pure aluminum drillings, antimony, and acid, and carry through the procedure as for an analysis.

The tin value of the iodate solution used is the weight of tin in the sample divided by the ml. of iodate required.

NOTES.—1. If so much elemental silicon is present that it would obscure the titration, filter the original solution, return to the flask with 0.25 g. of antimony and 1 g. of pure aluminum. Add 25 ml. of concentrated hydrochloric acid, then carry through as usual.

2. The titration may be made with standard iodine solution if preferred.

SPECIAL PROCEDURES

DETERMINATION OF METALLIC ALUMINUM

The formation of oxide film on finely divided aluminum during the process of manufacture is well known. For many purposes the metallic aluminum content of the powder is of importance, and it is customary to determine it either directly, or to determine the impurities and oxide, and take metallic aluminum by difference. The former procedure is more convenient and is generally adopted. The determination of impurities (iron, silicon and copper) for the difference method may be made by procedures similar to those used for metal in massive form,[23] except that prolonged fuming with sulfuric acid may be necessary to remove carbonaceous matter prior to the silicon determination. The direct determination of metallic, as distinguished from total, aluminum, has been made by several methods, practically all of which utilize the strong reducing action of the metal. Schulze [24] measured the volume of the hydrogen evolved by the reaction of an alkali on aluminum; Klemp [25] introduced weighing as water after combustion. Objection was raised to both these on the grounds that any silicon present would react with alkali in the same way as aluminum. This is correct, but the silicon content of aluminum powder is so small that the error arising from it is negligible.

Kohn-Abrest [26, 27, 28] suggested three methods. One was the hydrogen evolution method of Klemp and Schulze, with the substitution of hydrochloric acid for sodium hydroxide as the solvent; another depended upon the reduction of ferric salt to the ferrous condition and the titration of the reduced iron; in the third, the aluminum was volatilized in a non-oxidizing atmosphere as chloride by a stream of hydrogen chloride at an elevated temperature, and the total chlorine in the sublimate determined and calculated to metallic aluminum after applying correction for iron. The last named method is somewhat tedious, and the determination of aluminum is indirect; the ferric salt reduction is practically impossible to carry out without some side-reaction in which hydrogen is generated by action of aluminum upon the water present; the hydrogen evolution from hydrochloric acid possesses no advantage over that from alkalis and the action is less specific. Rhodin [29] assumed that 10% sodium hydroxide completely dissolved aluminum metal, but no aluminum oxide, and based a method upon this assumption. Bezzenberger [30] made a similar assumption concerning the action of bromine water, and proposed its use to differentiate between metallic and oxidized aluminum. As the various forms of oxidized aluminum differ markedly in their solubility, it seems improbable that these or any other methods of differential solution can be ap-

[23] Churchill, H. V., and Bridges, R. W., "Chemical Analysis of Aluminum" (1935).
[24] Schulze, F., Wagner's Jahresber., **10**, 23 (1864).
[25] Klemp, G., Z. anal. Chem., **29**, 388–9 (1890); J. Soc. Chem. Ind., **9**, 969 (1890).
[26] Kohn-Abrest, E., Ann. Chim. anal., **9**, 381–2 (1904); J. Chem. Soc., **86**, II, 844 (1904).
[27] Kohn-Abrest, E., Compt. rend., **147**, 1293–6 (1908); Bull. Soc. Chim., **5**, 207–17 (1908); C. A., **3**, 1130 (1909).
[28] Kohn-Abrest, E., Compt. rend., **149**, 399 (1909); Ann. chim. anal. appl., **14**, 285–9 (1909); C. A., **3**, 2916 (1909).
[29] Rhodin, J. G. A., Trans. Faraday Soc., **14**, 134–49 (1919); C. A., **13**, 1801 (1919).
[30] Bezzenberger, F. K., J. Ind. Eng. Chem., **12**, 78–9 (1920).

plicable to any considerable variety of materials. Faber and Stoddard [31] have proposed reduction of litharge by aluminum powder and weighing of the resulting lead button. This method appears simple and attractive, but tests in our laboratories show that side reactions occur which cause large errors. Several other authors have published procedures which are either identical with, or minor modifications of, the preceding.

For aluminum powder, the objections which have been raised against the hydrogen evolution and combustion method have little weight, and this method is used almost exclusively by the laboratories of the Aluminum Company of America.

DETERMINATION OF METALLIC ALUMINUM

Hydrogen Evolution Method

Apparatus.—A train, as shown in Fig. 3, consisting of the following units, is used, except that absorption tube (I) containing ascarite may be omitted:

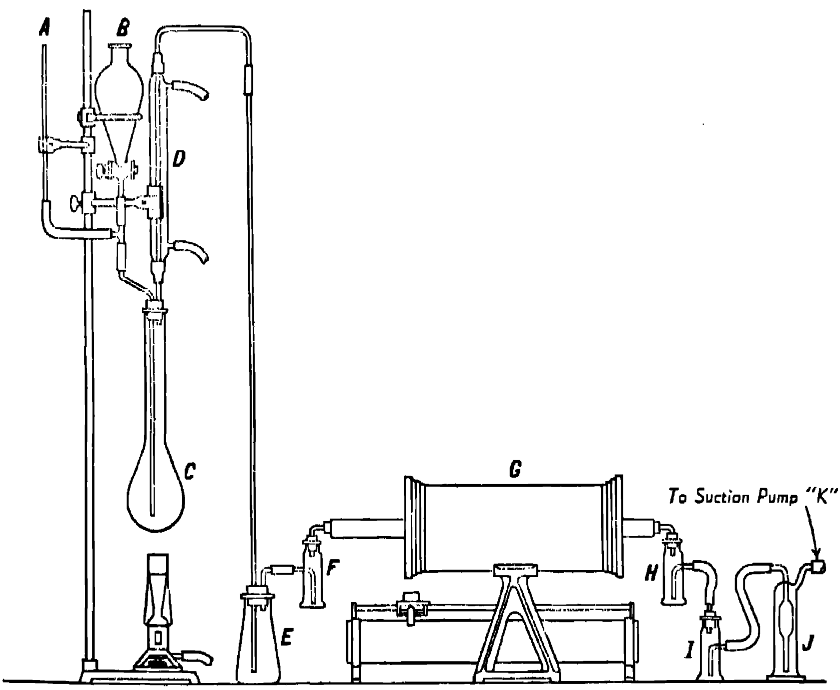


Fig. 3.—Apparatus for the Hydrogen Evolution Method.

A. Air inlet.
B. Separatory funnel.
C. Decomposition flask, 500 ml. Kjeldahl.
D. 10-inch reflux condenser.
E. Ammonia trap containing 1 : 1 sulfuric acid.

[31] Faber, H. B., and W. B. Stoddard, J. Ind. Eng. Chem., 12, 576–8 (1920).

F. Drying tube containing Dehydrite.

G. Combustion furnace. The tube should be filled with copper oxide to the inlet end, and the copper oxide held in place by a small asbestos plug. The tube should project from the furnace about 6 in. on the inlet side, so that the hydrogen comes in contact with cold copper oxide before entering the zone of reaction, and 2½ to 3 in. on the exit side, so that water will not condense, and the stopper will not be overheated.

H. Absorption tube containing Dehydrite.

I. Absorption tube containing Ascarite.

J. Guard bottle containing concentrated sulfuric acid.

K. (Not shown.) Suction pump.

A small capsule is also needed for the introduction of the sample. It may be conveniently made by cutting off a small vial about ¼ in. from the bottom.

Procedure.—Pass a current of air (approximately 5 bubbles per second) through the train for 30 minutes after bringing the furnace at 600° C. Remove and close the absorption tube, cool for 15 minutes, open momentarily, and weigh. Replace in the train, continue for 30 minutes more, cool for 15 minutes, open momentarily, and reweigh. A blank of 0.4 mg. or less is considered satisfactory. Weigh approximately 0.5 g. of sample in the capsule and place it in the decomposition flask. Add enough water to cover the bottom of the tube and 20 ml. of 20% potassium hydroxide solution. Continue passage of air at the same rate. When reaction begins to slow down, heat with a small flame until the sample is completely in solution and for 30 minutes thereafter. Close and disconnect the absorption tubes, cool for 15 minutes, open momentarily, and weigh. Deduct a determined blank. The gain in weight is due to water.

$$\text{Metallic aluminum} = \text{water} \times 0.998.$$

DETERMINATION OF ALUMINUM IN IRON AND STEEL[32]

The method is especially adapted for determination of aluminum in iron and steel, but may be extended to iron ores and materials high in iron.

Procedure. Solution.—Ten grams of iron or steel are dissolved by adding about 50 ml. of hot hydrochloric acid, 1 : 1, preferably in a platinum dish, covered with a platinum foil.

Precipitation.—When the solution of iron is complete, it is diluted to about 100 ml. and filtered free of carbon, silica, etc. Two grams of sodium phosphate are added and the solution neutralized with ammonium hydroxide or carbonate, then cleared by hydrochloric acid with about 1 ml. excess. Twenty ml. of acetic acid are now added and the solution diluted to 300 to 400 ml. with hot water and, on boiling, 10 grams of sodium thiosulfate added. The solution is boiled free of sulfurous acid (no odor of SO_2) about 20 to 30 minutes being necessary. The phosphate is filtered off and washed with hot water. It is again dissolved in a little hydrochloric acid and aluminum reprecipitated

[32] Arnold and Ibbotson, "Steel Works Materials." Stillman, "Engineering Chemistry." "A Rapid Method for the Determination of Aluminum in Iron and Steel." Chem. News, 61, 313. "On the Determination of Minute Quantities of Al in Iron and Steel," J. E. Stead, J. Soc. Chem. Ind., 956, 1889.

by neutralizing with ammonium hydroxide and adding about 1 gram of sodium phosphate together with 10 grams of sodium thiosulfate, following the above procedure. The precipitate will now be free of iron.

Ignition and Calculation.—The precipitate and filter are ignited wet, first over a low flame, then gradually increasing the heat to full blast of a Meker burner. The residue contains 22.11% Al or 41.78% of Al_2O_3.

Factor $AlPO_4$ to Al = 0.2211.

Factor $AlPO_4$ to Al_2O_3 = 0.4178.

NOTES.—Interfering substances. Copper may be removed by H_2S. Other members of this group will also be eliminated.

Manganese and nickel are eliminated together with small amounts of iron at the second precipitation.

Titanium may be estimated colorimetrically or separated from alumina.

Vanadium, if present, may be separated according to directions given in the chapter on Vanadium.

Chromium is eliminated by fusion of the mixed phosphates with Na_2CO_3, extraction with water, and precipitation of aluminum phosphate by adding ammonium acetate and sodium phosphate. Chromium remains in solution.

Other Methods.—L. Belasio adds crystalline tartaric acid to hold up the precipitation of other metals that commonly interfere. I. Ivanov neutralizes the slightly acid solution of aluminum with $Na_2S_2O_3$, then dilutes to 100 ml. adds KI in excess, then a 3% soln. of KIO_3 with additional KI until precipitation is complete. The excess of iodine is expelled by boiling and the $Al(OH)_3$ washed with neutral 3% NH_4NO_3 soln. and ignited as usual, to Al_2O_3. E. Schum (Chem. Zeit., **32**, 877, 1909) neutralizes the solution with NH_4OH just avoiding precipitation of $Al(OH)_3$. After dilution to 250 ml., 20 ml. 6% ammonium nitrite soln. are added, the solution boiled to expel NO_2, the $Al(OH)_3$ settled 20 min. and filtered and washed with ammonium nitrite solution and the precipitate ignited as usual to Al_2O_3.

DETERMINATION OF ALUMINUM, ALUMINA, AND TOTAL ALUMINUM IN STEEL

Apparatus.—Mercury cathode (Melaven cell).

Reagents.—Sulfuric acid (sp.gr. 1.84). 1–9 sulfuric acid. 1–3 hydrochloric acid. Sulfurous acid (distilled water saturated with sulfur dioxide), sp.gr. 1.02. Potassium pyrosulfate. Hydrogen peroxide, 3%. Ammonium chloride wash solution. Dilute 25 ml. hydrochloric acid, neutralize to methyl red with ammonium hydroxide, and dilute to one liter. Add 2 drops excess ammonium hydroxide. Methyl red indicator. Methyl orange indicator.

DETERMINATION OF ALUMINUM

Procedure.—Place 5 g. of sample in a medium sized beaker, add 55 ml. of 1–9 sulfuric acid, and cover. Warm until solution is complete, wash down sides of beaker and cover glass, filter into a 600-ml. beaker, and wash well with hot water. It is considered that the aluminum in the samples is in the filtrate and alumina is in the residue. Reserve the residue if it is desired to determine alumina or total aluminum. Dilute the filtrate to 200 ml., cool somewhat, add 50 ml. of sulfurous acid and neutralize with 1–1 ammonia using methyl orange as an indicator. Add the ammonia until the solution is yellow (a precipitate should be obtained). Add 20 ml. more of sulfurous acid and boil the solution until precipitation begins and for 10 minutes longer. The boiling is continued

until hydrolysis of iron begins. Filter rapidly using a large paper and wash with hot water. Using hot 1–9 sulfuric acid, dissolve the precipitate from the paper into the beaker in which the precipitation was made. Bring any oxides on the side of the beaker into solution. Add 2 drops of methyl red and ammonium hydroxide until the solution is just yellow. Then add concentrated sulfuric acid dropwise until the solution is red and 5 drops excess. Transfer to a mercury cathode and electrolyze using 2 ampere current until all the iron and other metals which will go into the mercury are removed. The deposition of iron and other metals will be hastened if a few drops of ammonium hydroxide are added to the electrolyte from time to time to reduce the acidity which builds up as the iron is deposited. When electrolysis is complete remove the electrolyte from the mercury cathode in the usual manner. Filter to remove any mercury or insoluble material and wash with water. Heat the solution to boiling, and just neutralize, using methyl red indicator. Warm to coagulate the precipitate, filter and wash well with ammonium chloride wash solution. Ignite in a weighed 10 ml. platinum crucible at 1050° C. for one hour. Cool, add four drops of concentrated sulfuric acid, and 15 drops of hydrofluoric acid. Evaporate cautiously to dryness, and ignite for 30 minutes at 1050° C. Cool and weigh. Deduct a determined blank.

$$\frac{Al_2O_3 \times 0.5291 \times 100}{\text{Weight of Sample}} = \%\ \text{Aluminum}$$

Determination of Alumina

Procedure.—Ignite the residue obtained when the sample was dissolved in a 10 ml. platinum crucible. Fuse it with a small amount of potassium pyrosulfate and take up with a few ml. of 1–9 sulfuric acid. Using the mercury cathode, finish the determination by the procedure as given for the determination of aluminum, except that a reprecipitation of aluminum hydroxide should be made.

$$\frac{Al_2O_3 \times 100}{\text{Weight of Sample}} = \%\ \text{Alumina}$$

Determination of Total Aluminum

Procedure.—Total aluminum may be determined by combining the solution of the insoluble residue with the filtrate containing the aluminum and carrying out the outlined procedure, or by calculation as follows:

$$Al + Al_2O_3 \times 0.5291 = \text{Total Aluminum}$$

Notes.—1. A weight of sample should be used which will give 1 mg. of alumina or more. For determination of high aluminum as in "Nitralloy," 0.5 g. is sufficient. In this case the separation of the major part of the iron before electrolysis may be omitted. The iron can be removed by electrolysis from any sample, however large the weight. The time required and formation of iron amalgam increases with the weight of sample and is somewhat inconvenient for large weights.

2. Aluminum can be precipitated in the electrolyte from which the iron has been removed with 8-hydroxyquinoline. Precipitation should be made after oxidation with hydrogen peroxide which prevents the interference of tantalum, columbium, molybdenum, titanium and vanadium. Aluminum can be determined then by ignition of the

aluminum oxine or by titration with thiosulfate or sulfuric acid as given in procedures A or B for Determination of Magnesium, page 47.

3. The alumina precipitate should be examined for phosphorus, vanadium, and titanium and, if present, they should be determined and the weight of alumina corrected accordingly.

4. If the aluminum, alumina, or total aluminum are too low to make satisfactory gravimetric determination, the "Aluminon" Colorimetric Method may be used. Transfer the electrolyte containing the aluminum, alumina or total aluminum from which the iron has been removed to a 100 ml. volumetric flask. Make the solution just acid to litmus paper and follow procedure as given for Determination of Aluminum in Animal Tissues and Foods, page 56.

$$\frac{Al_2O_3 \times .5291}{\text{Sample weight}} = \text{Aluminum}$$

DETERMINATION OF ALUMINUM IN BRONZE

Procedure in Analysis.—A sample weighing 0.5 to 1.0 g. is dissolved in 10 ml. of HNO_3 (2 : 1) and heated to expel nitrogen oxides. 50 ml. of water are added and the precipitate allowed to settle (oxide of Sn, P_2O_5 and some Cu) and then filtered. The filtrate is treated with 5 ml. H_2SO_4 and evaporated to fumes, then taken up with about 50 ml. of water and saturated with H_2S, and the precipitate filtered off. The filtrate containing the iron, aluminum, zinc, etc. is boiled to expel H_2S and oxidized by boiling with 5 ml. HNO_3. Iron and aluminum are now precipitated as hydroxides by addition of NH_4OH and filtered off and washing as usual. Iron and aluminum are separated by dissolving the hydroxides in a little HCl and neutralizing the free acid with Na_2CO_3 solution. Any permanent precipitate is dissolved by a few drops of HCl. For each 0.1–0.2 g. of the metals present the solution is diluted to about 250 ml. and an excess of $Na_2S_2O_3$ is added. Aluminum hydroxide is precipitated, iron remains in solution in the ferrous form. $2AlCl_3 + 3Na_2S_2O_3 + 3H_2O = 2Al(OH)_3 + 3SO_2 + 3S + 6NaCl$. The $Al(OH)_3$ is filtered off and washed with hot water, then dried and the hydroxide and filter ignited separately, the ash of the paper added to the alumina and the ignition continued until a constant weight is obtained. An electric furnace or a Meker burner may be used to expel the combined water. Weigh as Al_2O_3.

$$Al_2O_3 \times 0.5291 = Al.$$

COLORIMETRIC AURIN TRICARBOXYLIC METHOD (ALUMINON)

The solution should be free from iron, beryllium and substances precipitated by ammonium carbonate and salts forming colored solutions.

Procedure.—The dilute HCl solution free from interfering substances diluted to about 25 ml. and containing about 0.5 ml. free acid, add 3 ml. glacial acetic acid, 5 ml. of 2% solution of the ammonium salt of "Aluminon" reagent, and while stirring add drop by drop a 10% solution of ammonium carbonate in dilute ammonium hydroxide until there is an excess of about 10 ml. Compare the color with standard solutions containing known amounts of aluminum.

NOTES.—Iron interferes and must be entirely absent. Beryllium gives a similar lake. Si, Sb, Pb, Bi, Sn^4, Ti, Hg^2 give white precipitates. SO_2 and H_2S cause a fading color.

See also "Determination of Aluminum in Plants," O. B. Winter and C. D. Bird, J. Am. Chem. Soc., **51**, 2721–2731, 1929; and "Occurence and Det. of Aluminum in Foods," G. J. Cox, E. W. Schwartz, R. M. Hann, R. B. Unangst and J. L. Neal, Ind. and Eng. Chem., **24**, 4, 1932.

ANALYSIS OF ANIMAL TISSUES AND FOODS

DETERMINATION OF ALUMINUM

Reagents Required.—Hydrochloric acid, 6 M (constant boiling). Sulfuric acid, concentrated. Sulfuric acid, 2.3 M. Ammonium acetate, 5 M. Ammonium chloride, 5 M. Sodium acetate, 3 M. Sodium phosphate, primary, 1 M. Ferric sulfate, 0.1 M. Distilled water to 500 ml.

Ammonium carbonate, 1.6M. Aluminon, ammonium aurintricarboxylate, 0.1%. Thioglycollic acid. Bromthymol blue, .04%. Bromcresol green, .04%. Thymol blue, .04%.

Combined reagent made up of 200 ml. ammonium chloride, 5 M. 200 ml. ammonium acetate, 5 M. 80 ml. aluminon, 0.1%. 60 ml. hydrochloric acid, 6 M. Distilled water to 1 liter.

Permanent Color Standard.—5 ml. thymol blue, .04%. 8 ml. hydrochloric acid, 6 M. Distilled water to 500 ml.

Standard Solution.—Potassium aluminum sulfate, 1 ml. = .01 mg. Al 0.1759 g. $Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$/l.

Standard Solution.—Ferric sulfate, 1 ml. = 0.001 mg. Fe. 7.2 mg. $Fe_2(SO_4)_3$/l.

Ashing and Solution of Sample.—A suitable quantity of material is weighed into a platinum dish. If moist, the material is dried at 110° C. The dish and contents are placed in a cold muffle furnace and the temperature slowly raised to 500–550° C. and held at this temperature until all carbon has disappeared. A slow stream of oxygen passing through the furnace, or leaving the door open slightly, is a material aid in the ashing of the sample. When cool, the ash should be roughly weighed, if it contains much calcium phosphate, since the volume must later be adjusted for the calcium phosphate content. Add 5 ml. concentrated hydrochloric acid to the ash and wash down the sides of the dish with 25–50 ml. hot water. Cover and evaporate to dryness. Take up with 5 ml. 6 M hydrochloric acid and about 50 ml. hot water. Boil to dissolve the soluble matter and filter through a small paper. A centrifuge may be used if desired. Wash filter, place in a small platinum crucible and ignite.

Volatilize the silica in the usual way, and fuse any insoluble matter in a small amount of a molecular mixture of sodium and potassium carbonates. Dissolve the fusion in the main solution.

Separation of Iron and Aluminum from Other Constituents.—If the sample is a carcass, or other material high in calcium phosphate, take an aliquot of such a magnitude that the calcium phosphate content will not be greater than 3.0 g. per 100 ml. of solution. Transfer to a small Erlenmeyer flask, add 0.5 ml. concentrated nitric acid, 1 ml. 0.10 M ferric sulfate and boil almost to dryness. Take up with hot water, cool somewhat, add 5 ml. 1 M primary sodium phosphate (1 ml. is sufficient for a carcass sample), and 0.5 ml. bromphenol blue indicator, .04%. Add ammonium hydroxide (1 : 1) from a burette till a precipitate begins to form, then finish neutralizing to a pH of 4.2 with 3 M sodium acetate. When much calcium is present, this end point must be carefully controlled, and the neutralization must be accompanied with vigorous shaking, otherwise, calcium phosphate will precipitate with the iron and aluminum. Transfer the contents of the flask to a 50 ml. centrifuge tube and centrifuge 5 minutes at 1800 r.p.m. Decant the supernatant liquid. Add 2.5 ml. 2.3 M sulfuric acid and about 25 ml. hot water to the precipitate. Stir until the precipitate dissolves. If much calcium was originally present it is advisable to transfer the solution to the small Erlenmeyer flask, add 5 ml. 1 M primary sodium phosphate and repeat the precipitation.

Separation of Iron from Aluminum—Electrolytic Method.—The cell used in this separation is a glass cylinder 2 inches in diameter and 4 inches long. The bottom third of the tube is drawn down to a cone to which a two-way stopcock is sealed. One leg of the stopcock serves as the connection for the mercury cathode, while the other leg is used to draw off the finished solution. The anode is of platinum and has an area of 4 sq. cm. A current of 1.5–2.0 amperes is used corresponding to a current density of 37–50 amperes per square decimeter. (See Fig. 2, p. 47.)

Transfer the solution of the phosphates in sulfuric acid to the cell and electrolyze 1 hour and 30 minutes. Run the mercury off into its reservoir, then draw off the solution and rinse the cell. Receive the solution in a 100 ml. volumetric flask. Make the solution just acid to litmus paper, make up to the mark and mix. To test for iron, place a 10 ml. portion of the solution in a graduated LaMotte test tube, add 2 drops of thioglycollic acid and mix, add 1 ml. 6 M ammonium hydroxide and mix again. Compare with similarly prepared standards containing known amounts of iron; usually 0.001 and 0.002 mg. suffice. Compute and record the iron content of whole solution. If this is greater than one-tenth the amount of aluminum subsequently found, it will cause an appreciable error in the determination.

Determination of Reagent Additions for Aluminum Determinations.—Place a 20 ml. aliquot of the solution in a 250 ml. glass-stoppered Erlenmeyer flask. From a burette, add 25 ml. of the combined reagent and mix. The pH of the resulting solution should be 5.0. This is determined by placing 10 ml. in a LaMotte graduated test tube, adding 0.5 ml. of .04% bromcresol green and comparing with the color standards. A variation of 0.5 pH units is permissible, but not desirable. Place another 20 ml. aliquot of the solution in a 250 ml. flask, add 25 ml. of the combined reagent, suspend a small Hopkins type reflux condenser in the neck of the flask and boil very gently exactly

one minute. Allow the flask, with condenser in place, to cool 10 minutes. Remove condenser, stopper the flask, and cool to room temperature in running water. From a burette, add 5 ml. of 1/6 M ammonium carbonate to the flask, shaking gently. Stopper the flask and shake it uniformly 20 times. Allow to stand 20 minutes. Determine the pH of this solution using a 10 ml. portion to which is added 0.5 ml. of bromthymol blue .04% solution. Compare the color with standards in a block type comparator. The pH of the solution at this point should be between 7.0 and 7.3, 7.1 being the optimum. If the pH is outside this range, change the addition of carbonate for the later determinations by 0.25 ml. for each 0.1 unit of pH variation from 7.1. The shaking of the solution, after the addition of carbonate, must be uniform, as this exercises considerable control over the final pH.

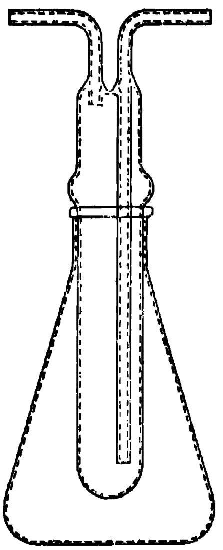


FIG. 4.—Flask and Condenser for Lake Development.

Determination of Aluminum

Place another 20 ml. aliquot of the solution in a 250 ml. glass-stoppered Erlenmeyer flask, add 25 ml. of the combined reagent, insert the reflux condenser and proceed exactly as in the determination of reagent additions. Add the previously determined amount of 1.6 M ammonium carbonate and shake 20 times. Allow to stand 20 minutes. Then compare the color of the sample with that of a simultaneously developed standard containing a known amount of aluminum, by means of a Duboscq type colorimeter. Set the standard at 30 mm. and vary immersion of the plunger in the sample until a match is obtained. Calculate the amount of aluminum present in the aliquot by the following relation:

$$\frac{\text{Weight Aluminum in Standard}}{\text{Weight Aluminum in Sample}} = \frac{\text{Depth of sample layer}}{\text{Depth of standard layer}}$$

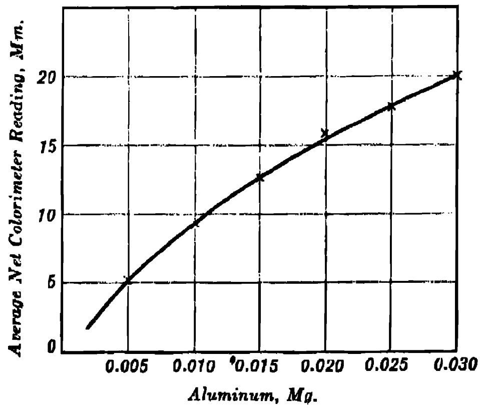


FIG. 5.—Net Colorimeter Readings Obtained With Added Aluminum.

Check the pH of the solution at this point. A blank should be obtained and deducted. It is desirable to have the standard between 50 and 200% of the aluminum content being measured.

If a large number of determinations are to be made over a period of time it is advantageous to prepare a curve for the relation between the colorimeter readings and the amount of aluminum present.

Suitable amounts of aluminum, viz., .002, .005, .010, .015, .020, .025 and .03 mg. multiplied by 5 are taken and treated as in the method, adding 5 ml. 6 M hydrochloric acid and proceeding from the point Separation of Iron and Aluminum from Other Constituents. It is absolutely necessary that these standards be carried through from this point, otherwise a different tint will be obtained when the final color is developed. The color of these standards is compared with a portion of the Permanent Color Standard. The plunger in the standard aluminum solution is set at 30 mm. and the depth of the other prism is varied to obtain a match and its depth read on the scale. After deducting a determined blank, these depths are used as ordinates and the amounts of aluminum as the abscissa for points on the curve.

DETERMINATION OF ALUMINUM IN SMALL QUANTITIES[33]

(A) GENERAL METHOD FOR ACCURATE WORK

Solutions Required

"Electrolytic Solution."—Mix 300 ml. of HNO_3 (sp.gr. 1.42), 1700 ml. of distilled water, and 500 ml. of H_2SO_4 (sp.gr. 1.84).

Acidified H_2S Water for Washing.—Dilute 10 ml. of HCl (sp.gr. 1.20) with 1000 ml. of distilled water and saturate with H_2S.

Phenylhydrazine Solution for Washing.—Add saturated SO_2 water to a few cubic centimeters of phenylhydrazine until the crystalline sulfite first formed is redissolved, and then add phenylhdrazine, drop by drop, with vigorous agitation, until the odor of SO_2 is no longer perceptible; dilute 5 to 10 ml. of this solution with 100 ml. of hot water and allow to remain at the boiling point for a few minutes so as to get rid of the excess SO_2.

NH_4Cl Solution for Washing (2 per cent).—Mix 30 ml. of HCl (sp.gr. 1.20) with 200 ml. of distilled water, add methyl red, neutralize with NH_4OH until the solution changes to a distinct yellow, and then dilute to 1000 ml. with water.

[33] A. W. Brown, Chief Analyst, National Lead Co.

Method.—Dissolve 1 g. of brass or bronze in 35 ml. of "electrolytic solution," dilute with 100 ml. of distilled water and remove copper by electrolysis. Evaporate the electrolyte to fumes of SO_3. (If much tin is present, boil the sulfuric acid solution vigorously for a few minutes.) Cool, and dilute with 100 ml. of water. Filter off $PbSO_4$ and any tin which may be precipitated at this point, washing with hot water. Dilute the filtrate to at least 200 ml.

Pass H_2S into the filtrate for 30 minutes. This will precipitate any copper, lead, tin, arsenic, or antimony which may be present. Allow the sulfides to settle, and filter, washing with acidified H_2S water. Boil the filtrate to one-half volume to expel H_2S, add 3 ml. HNO_3 (sp.gr. 1.42) and boil for a few minutes to oxidize iron.

Precipitate iron and aluminum according to the following:[34] Add 10 ml. of HCl (sp.gr. 1.20) and just neutralize with NH_4OH, using methyl red as an indicator. Boil for two minutes and filter, washing with hot NH_4Cl (2 per cent). Dissolve the precipitate from the paper with boiling hot HCl (1 : 1) and wash alternately with hot water and HCl (1 : 1) into the beaker in which the precipitation was made. Reprecipitate the iron and aluminum following the same precedure as before.

Dissolve the precipitate again with hot HCl (1 : 1), dilute to 100 ml. with water, make just ammoniacal, then only acid enough to hold iron in solution. Add sufficient saturated solution of ammonium bisulfite to reduce the iron (5 to 20 drops). Add a few drops of methyl orange, quickly bring to neutrality with NH_4OH, and then add 6 to 7 drops of HCl (1 : 1) in excess. Finally, add from 1 to 3 ml. of phenylhydrazine and stir until the precipitate becomes flaky. The supernatant liquid should be plainly acid to litmus and the precipitate may be colored owing to organic matter. Filter and wash with phenylhydrazine wash solution. Ignite in a weighed platinum crucible, finishing with the blast for 5 minutes. Weigh as Al_2O_3. The weighing should be made rapidly and with the crucible covered as Al_2O_3 is somewhat hygroscopic.

NOTES.—1. For small amounts of aluminum, a 5-g. sample should be used. In this case dissolve in 60 ml. of "assay solution" of the following proportions:

7 volumes HNO_3 (sp.gr. 1.42),
10 volumes H_2SO_4 (sp.gr. 1.84),
25 volumes H_2O.

2. When phosphorus is present the final precipitate will be $Al_2O_3+P_2O_5$. In this case it is necessary to fuse the residue with Na_2CO_3, dissolve with hot water, acidify with HNO_3, and determine phosphorous in accordance with the "Determination of Phosphorus by the Alkalimetric Method." The phosphorus is calculated to P_2O_5 and subtracted.

3. For accurate work the Al_2O_3 residue is treated with HF and H_2SO_4 for the removal of possible SiO_2.

4. Ammonium bisulfite solution may be prepared by saturating cold NH_4OH (1 : 1) with SO_2 until yellow.

5. This method is especially satisfactory for small amounts of aluminum in brass or bronze since no reagents are used which may contaminate the precipitate with aluminum, iron or silica. A precipitate with phenylhydrazine gives positive indication of the presence of aluminum.

[34] Blum: U. S. Bureau of Standards Scientific Paper, No. 268, 1916; J. Am. Chem. Soc., **38**, p. 1282 (1916).

(B) RAPID METHOD FOR CONTROL WORK

Solutions Required

Sodium Hydroxide Solution (2.5 per cent).—Dissolve 25 g. of NaOH (free from aluminum) in water and dilute to 1000 ml.

Sodium Sulfide Solution.—Dissolve 150 g. of NaOH (free from aluminum) in 1000 ml. of water, saturate 500 ml. of this solution with hydrogen sulfide, and mix with the remaining 500 ml. of solution.

Dilute Hydrochloric Acid (1 : 3).—Mix 200 ml. of HCl (sp.gr. 1.20) with 600 ml. of water.

Acidified Hydrogen Sulfide Water.—Dilute 10 ml. of HCl (sp.gr. 1.20) with 1000 ml. of water and saturate the solution with hydrogen sulfide.

Ammonium Chloride Solution (2 per cent).—Mix 30 ml. of HCl (sp.gr. 1.20) with 200 ml. of water, add methyl red, neutralize with ammonia until the solution changes to a distinct yellow, and then dilute to 1000 ml. with water.

Method.—Dissolve 2 g. of the sample in 20 ml. of HCl (sp. gr. 1.20) and 5 ml. of HNO_3 (sp.gr. 1.42). Boil the solution to expel chlorine, and dilute with 50 ml. of water. Nearly neutralize the cold solution with NaOH solution (2.5 per cent, or stronger if much free acid is present), and pour it slowly and with constant shaking into a 500 ml. volumetric flask containing 100 ml. of sodium sulfide solution. Dilute to the mark with NaOH solution (2.5 per cent) and mix thoroughly. Filter on a large, dry, No. 42 Whatman filter paper (or its equivalent) and keep the paper well filled with the solution lest iron be oxidized and dissolved. Reject the first 20 to 25 ml., and catch exactly 250 ml. which will represent 1 g. of sample. In routine analyses of material containing not more than 1 per cent of aluminum, the aliquot portion can be gathered in a 250-ml. graduate.

Transfer the aliquot to a 600-ml. beaker, neutralize the solution with dilute HCl (1 : 3), and finally add 25 ml. in excess. Digest at 40 to 60° C. for 1 hour, filter, and wash the paper and precipitate with acidified H_2S water.

Boil the filtrate and washings to expel H_2S, add a few drops of methyl red indicator, and then dilute ammonia (1 : 2) until the solution is just distinctly yellow. Boil for 1 to 2 minutes and filter at once through a small filter. Wash the beaker, paper, and precipitate two or three times with hot NH_4Cl solution (2 per cent) and discard the filtrate. Dissolve the precipitate in 200 ml. of hot dilute HCl (1 : 3), wash the filter thoroughly with small portions of hot water, and reserve it for the second filtration. Dilute the filtrate to 50 ml., add methyl red, and precipitate with dilute ammonia (1 : 2) as before. Filter, wash with hot NH_4Cl solution (2 per cent), ignite, and weigh.

The ignited residue is prone to carry silica and must be purified before weighing as follows: Add one or two drops of water, one drop of diluted H_2SO_4, and 1 to 5 ml. of HF. Evaporate to dryness, increase the heat slowly, and finally heat with a blast lamp or its equivalent. Weigh as Al_2O_3. The weight of Al_2O_3 corrected for the blank and multiplied by 52.91 gives the percentage of aluminum.

Notes.—The first aluminum hydroxide precipitate will carry down some NaCl and much of any silica that was dissolved in the NaOH solution; hence, it is not safe to omit the second precipitation and the HF treatment. There is no attack on the glassware during the short contact with the weak, cool, alkaline solution. It is, of course, pre-

ferable that the NaOH be free from aluminum. The most satisfactory test for it lies in running an analysis with non-ferrous alloys containing no aluminum. Direct test, by acidification followed by precipitation with ammonia, is sufficient if no precipitate is obtained, but is of doubtful value in case one appears, for it may contain other elements, such as iron, which do not affect the results.

If phosphorus is known to be present, the method should be followed through the first addition of ammonia. If aluminum is indicated, re-acidify the solution with HCl, add macerated paper, two drops of methyl orange, and 10 ml. of a solution of diammonium phosphate (10 per cent). Render the solution just ammoniacal, then just restore the pink color with dilute HCl (1 : 3), heat to boiling, and add 30 ml. of a solution of ammonium acetate (25 per cent). Boil for 5 minutes, filter on an 11-cm. No. 42 Whatman or similar filter paper, and wash with hot NH_4NO_3 solution (5 per cent) until 5 ml. of the washings no longer give a test for chlorides with acidified $AgNO_3$. Ignite in platinum or procelain, heat at approximately 1100° C. for 10 minutes, and weigh as $AlPO_4$. This method is not strictly accurate on account of the uncertain composition of the phosphate, but is sufficiently accurate for all but the most painstaking analyses.

ANTIMONY

Sb ***at.wt.*** **121.76;** ***sp.gr.*** **6.62;** ***m.p.*** **630° C.;** ***b.p.*** **1440° C.;** ***oxides*****,** Sb_2O_3, Sb_2O_4, Sb_2O_5

Antimony occurs free in nature, but more commonly as gray or black or iridescent sulfide, Stibnite, Sb_2S_3, the chief commercial source of antimony. It occurs combined with the heavy metals in form of sulfoantimonides and antimonides.[1]

DETECTION

Hydrogen Sulfide precipitates the orange-colored sulfide of antimony from fairly concentrated hydrochloric acid solutions (1 : 4) in which several members of the group remain dissolved. Arsenic is also precipitated. The latter may be removed by boiling the solution containing the trichloride, $AsCl_3$ being volatile.

If antimony is already present as a sulfide, together with other elements of the hydrogen sulfide group, it may be dissolved out by treating the precipitate with sodium hydroxide, potassium hydroxide, sodium sulfide, ammonium polysulfide in solution. Antimony sulfide is reprecipitated upon acidifying the filtrate. Arsenic and tin will also be precipitated with antimony if they are present in the original precipitate. Should a separation be necessary, the precipitate is dissolved with hot concentrated hydrochloric acid, with the addition of crystals of potassium chlorate, from time to time, until the sulfides dissolve. The solution is placed in a Marsh apparatus, pure zinc added and the evolved gases passed into a neutral solution of silver nitrate. The black precipitate of silver antimonide and metallic silver are filtered off, washed free of arsenious acid, and the antimonide dissolved in concentrated hydrochloric acid (silver remains insoluble). The orange-colored antimony sulfide may now be precipitated by diluting the solution with water and passing in H_2S gas to saturation.

[1] Compounds of antimony were employed in early times by the Hebrews. Metallic antimony alloys were used by the Chaldeans in their ornamental vessels, while compounds of antimony are known to have been used by the Chinese centuries ago. Antimony is now used in a variety of commercial products, in alloys, in paints, in rubber, etc.

Minerals which contain antimony, when heated alone or with 3 to 4 parts of fusion mixture (K_2CO_3 and Na_2CO_3), on charcoal, yield dense white fumes, a portion of the oxide remaining as a white incrustation on the charcoal. A drop of ammonium sulfide placed upon this sublimate gives a deep orange stain.

Hydrolysis.—Most of the inorganic antimony salts are decomposed by water, forming insoluble basic salts, which in turn break down to the oxide of antimony and free acid. An excess of tartaric acid prevents this precipitation.

Traces of Antimony.[2]—Nascent hydrogen liberated by the action of zinc and hydrochloric or sulfuric acid reacts upon antimony compounds with the formation of stibine. This gas produces a black stain on mercuric chloride or silver nitrate paper. Details of the procedure are given under the quantitative method for determining minute amounts of antimony.

Distinction between Antimonous and Antimonic Salts.

Chromates form with antimonous salts green chromic salts and antimonic salts.

Potassium Iodide reduces antimonic salts, free iodine being liberated.

ESTIMATION

In the decomposition of the sample provision must be made for ores, alloys such as Britannia metal, bearing and antifriction metals, type metal, hard lead, paints, vulcanized rubber, organic products, etc.

In the analysis of minerals some antimony would be volatilized, a part would remain with silica as the oxychloride, while some would be found with the alumina precipitate, unless provision had been made for its previous separation with H_2S in acid solution. These facts should be kept in mind in preparing samples for determining antimony.

PREPARATION AND SOLUTION OF THE SAMPLE

In dissolving the substance containing antimony it must be remembered that metallic antimony is practically insoluble in cold dilute hydrochloric, nitric

[2] See K. Heller, Mikrochemie **14**, 369 (1934) for a summary of microchemical tests. Potassium iodide and organic bases such as antipyrine, brucine, 2-amino pyridine, give distinctive color reactions with traces of antimony. Gutzeit and Weibl, Chem. Abstracts, **29**, 2471 (1935) treat mixed tin group sulfides with aqua regia, evaporate with HCl, place 1 drop of solution on filter paper, add 5 drops of 35% formaldehyde and after 2–3 minutes 1 drop of KI-antipyrine reagent. A yellowish brown stain indicates antimony. For other tests see Korenman, Z. anal. Chem., **99**, 402 (1934); **97**, 418 (1934). The antipyrine reagent gives a golden yellow ppt. with Sb^{III} and a brick red ppt. with Sb^{V} and serves to distinguish between the two forms according to Duquenois, Compt. rend., **197**, 339 (1933); Chem. Abstracts, **27**, 5675 (1933).

or sulfuric acid and the oxides, Sb_2O_3 or Sb_2O_5, are precipitated in concentrated nitric acid. The element, however, is readily soluble in hydrochloric acid containing an oxidizing agent, such as nitric acid, potassium chlorate, chlorine, bromine, etc. The oxides of antimony are soluble in hydrochloric acid and the caustic alkalies.

The element is soluble in hot concentrated H_2SO_4. In the decomposition of the sample the volatility of the chlorides must be kept in mind. This begins as low as 110° C. (b.p. $SbCl_3$ 223° C.; $SbCl_5$ 140° C.). Also the fact that the oxychloride of antimony will remain with silica unless dissolved out with HCl of sufficient concentration.

Solution of Sulfide Ores, Low-grade Oxides, etc.[3]

0.5 to 1 gram of the finely ground ore, placed in a Kjeldahl flask, is mixed with 5 to 7 grams of granular or powdered potassium sulfate, and 10 ml. of concentrated sulfuric acid. About 0.5 gram of tartaric acid, or a piece of filter paper, is added to reduce arsenic and antimony and the mixture heated, gradually at first, and then with the full Bunsen flame. The heating is continued until the carbon is completely oxidized and most of the free acid driven off, leaving a clean fusion but not to complete expulsion of H_2SO_4. The melt is now cooled over the bottom and sides of the flask by gently rotating during the cooling.

About 50 ml. of dilute hydrochloric acid (1 : 1) are added and the melt dissolved by warming gently. The contents of the Kjeldahl flask are transferred to an Erlenmeyer flask, the Kjeldahl being rinsed out with 25 ml. of concentrated hydrochloric acid. Arsenic sulfide may now be precipitated with H_2S from the strongly acid solution, whereas antimony, etc., remain in solution. The sulfide is filtered off through a double filter, that has been moistened with hydrochloric acid (2 : 1), a platinum cone supporting the filter to prevent its breaking. The flask is rinsed out with hydrochloric acid (2 : 1). The precipitate is washed at least six times with the acid. Antimony passes into the filtrate together with other elements of the ore.

The filtrate is diluted with double its volume of warm water and then is saturated with hydrogen sulfide. Antimony sulfide, together with other elements of the Hydrogen Sulfide Group, will precipitate. These are washed with hydrogen sulfide water. Antimony sulfide may now be dissolved by addition of sodium sulfide and caustic solution (separation from Cu, Pb, Cd, Bi, etc.) (5 to 10 ml. of a mix of 60 grams Na_2S with 40 grams of NaOH diluted to 1000 ml.).

The solution containing the antimony is treated with about 2 grams of potassium sulfate and 10 ml. of concentrated sulfuric acid and heated as before, to destroy liberated sulfur and expel most of the free acid. The melt is dissolved in hydrochloric acid, and the antimony titrated according to one of the volumetric procedures given under "Volumetric Methods."

Note.—An insoluble residue remaining from the acid extraction of the first melt may be dissolved by fusion with sodium hydroxide and extraction of the melt with hot water. If a precipitate forms when this alkaline solution is acidified with hydrochloric acid, the presence of barium sulfate is indicated.

[3] Method of A. H. Low modified.

Decomposition of the Ores by Fusion with Sodium Hydroxide.

Oxides.—0.5 to 1 gram of the powdered ore is mixed with about 10 grams of sodium hydroxide and placed in a thin-walled iron crucible of 60 ml. capacity. It is advisable to fuse a portion of the alkali hydroxide in the crucible with a pinch of potassium nitrate and then add the ore mixed with the remainder of the sodium hydroxide. The covered crucible is heated until the fusion becomes homogeneous. The melt is poured out on a large nickel crucible cover or shallow dish. On cooling, the cake is detached and placed in a casserole containing water, any adhering cake on the cover, or melt remaining in the iron crucible, being dissolved with dilute hydrochloric acid and added to the sample in the casserole. About 30 to 40 ml. of concentrated hydrochloric acid are now added and the mixture heated (casserole covered) until the melt has dissolved. Two to 3 grams of tartaric acid having been added to keep antimony dissolved, the solution is diluted to about 300 ml., and antimony is then precipitated as the sulfide with hydrogen sulfide. The treatment of the precipitate at this stage has been given in the "Solution of Sulfide Ores."

Sulfides.—Howard and Harrison[4] recommend the following procedure for fusion of sulfide ores with caustic: 0.5 gram of the powdered ore is fused with a mixture of 8 grams of sodium carbonate and sodium peroxide, 1 : 1, in a nickel crucible. The cooled melt is dissolved with sufficient hydrochloric acid to neutralize the alkali and about 15 ml. of concentrated acid added in excess. The solution is diluted to 250 ml., antimony being kept in solution by addition of potassium chlorate. An aliquot portion of the solution is taken, antimony reduced by metabisulfite and titrated with iodine.

Treatment of Speisses, Slags, Mattes, etc.[5]—0.5 to 2 grams of the sample is treated with 10 to 15 ml. of concentrated nitric acid and the mixture evaporated to dryness. Fifteen ml. of concentrated hydrochloric acid are added and the sample transferred to a 350-ml. flask, additional hydrochloric acid being used to wash out the beaker. Arsenic is precipitated from the concentrated acid solution as the sulfide, and antimony determined in the filtrate.

Solution of Alloys.—Alloys are generally decomposed by treatment with mixtures of hydrochloric acid together with an oxidizing agent—nitric acid, potassium chlorate, bromine, etc. The subject is taken up in detail in the chapter on alloys.

Care must be exercised to prevent volatilization of the chlorides, as has been stated in the introductory paragraph.

Alloys of Antimony, Lead, and Tin.—0.5 to 1 gram of the finely divided alloy is warmed with 100 ml. of concentrated hydrochloric acid until the action subsides. Solid iodine is now added, in small quantities at a time, until the alloy completely dissolves. The excess of iodine is now removed by boiling, and the small amount of free iodine remaining is neutralized with a few drops of a weak solution of sodium thiosulfate. Although tin is oxidized to the higher state, antimony is not oxidized by iodine in acid solution beyond the trivalent form. The solution may now be titrated with standard iodine is presence of an excess of sodium bicarbonate according to the procedure given under the volumetric methods.

[4] Pharm. Jour., 83, 147, 1909.
[5] H. E. Hooper's method.

Hard Lead.—The method of solution and titration is given under "Potassium Bromate Method for Determining Antimony."

ORGANIC COMPOUNDS

Fuming sulfuric acid and 30% hydrogen peroxide decomposes organic compounds containing antimony and other metallic elements rapidly and completely.[6] This mixture is said to be superior to sulfuric acid—potassium permanganate, sulfuric-nitric acid, or hydrochloric-perchloric-persulfate mixtures.

Procedure.—A sample containing approximately 0.1 g. of the element to be determined is placed in a Kjeldahl flask with 7 to 10 ml. of 15% fuming sulfuric acid (or ordinary conc. acid if the substance is easily decomposed). The substance is dissolved, if possible, by a gentle warming. Thirty per cent hydrogen peroxide (superoxol) is added drop by drop down the inside surface of the flask which is agitated gently. The addition of hydrogen peroxide is continued until the solution is at most straw colored. Then the mixture is warmed until fumes of sulfur trioxide are abundant. Sometimes more hydrogen peroxide is needed to decolorize the solution; total requirement 1 to 5 ml. Antimony and arsenic go into solution as arsenate or antimonate. Any suitable gravimetric or volumetric method may be used in the determination. The method is also applicable to the determination of bismuth, silver, germanium or mercury; in the last case a reflux condenser is used if the compound also contains iodine.

SEPARATIONS

Separation of Antimony (together with Members of the Hydrogen Sulfide Group) from Iron, Chromium, Aluminum, Cobalt, Nickel, Manganese, Zinc, the Alkaline Earths, and Alkalies.—The acid solution of the elements is saturated with hydrogen sulfide, the elements of the Hydrogen Sulfide Group are precipitated as sulfides, the other elements remaining in solution. Antimony sulfide may be precipitated from an hydrochloric acid solution containing 15 ml. of concentrated acid per 100 ml. of solution; lead and cadmium are incompletely precipitated.

Separation of Antimony (together with Arsenic and Tin) from Mercury, Copper, Bismuth, Cadmium, and Lead.—The sulfides of antimony, arsenic, and tin are soluble in a mixture of sodium hydroxide and sodium sulfide, the soluble sulfo salts being formed, mercury, copper, bismuth, cadmium, and lead remaining as insoluble sulfides. The following procedure may be used for alloys free from members of other groups. The acid solution is treated with 3 to 5 grams of tartaric acid and diluted slightly (more tartaric acid being added if the solution becomes turbid), then poured into 300 ml. of a mixture of sodium sulfide and sodium hydroxide (150 ml. of the mix described under "Solution of Sulfide Ores" diluted to 300 ml.). The mixture is warmed and the insoluble sulfides allowed to settle out. The solution is filtered free of the precipitate and the latter washed. The filtrate is acidified with hydrochloric or sulfuric acid and saturated with hydrogen sulfide. The sulfides of

[6] Tabern and Shelberg, Ind. Eng. Chem., Anal. Ed. 4, 401 (1932).

arsenic, antimony and tin are now filtered off and treated as described later.

Separation of Arsenic, Antimony, and Tin.—Method 1. The sulfides may be dissolved in concentrated hydrochloric acid by addition of potassium chlorate to oxidize the sulfur to sulfuric acid. This oxidation may be effected in the alkaline solution of the sulfo salts by addition of 30% hydrogen peroxide in small portions until the yellow solution is completely decolorized and then 1 to 2 ml. in excess, the solution then boiled to oxidize completely the sulfides to sulfates and to remove the excess of peroxide. The solution is then acidified, the precipitation of the sulfides and the subsequent filtration and resolution being avoided.

Removal of Arsenic.—This may be accomplished by volatilizing arsenic as arsenic trichloride in a concentrated hydrochloric acid solution by boiling. If arsenic is to be determined the procedure given under the chapter on arsenic is followed, the arsenic being distilled in a current of hydrochloric acid gas. If arsenic is not desired it may be expelled by reducing the solution with sodium metabisulfite or potassium iodide and boiling. Antimony and tin remain in the concentrated acid solution.

The separation of arsenic from antimony and tin may be effected by removal of the former in a concentrated hydrochloric acid solution as described under the section "Preparation and Solution of the Sample," arsenic being precipitated by hydrogen sulfide, whereas antimony and tin remain in solution.

The temperature should be kept below 108° C., otherwise $SbCl_3$ will start to volatilize (110° C.).

Separation of Antimony from Tin.—Upon the removal of arsenic, antimony may be determined directly in the presence of tin by one of the volumetric methods given later. If a gravimetric separation is desired, it may be made according to a modification of Clark's method,[7] which depends upon the fact that antimony is completely precipitated from a solution containing oxalic acid, by hydrogen sulfide, whereas tin is not. The tin must be in the stannic form, otherwise the insoluble crystalline stannous oxalate will form.

If the mixture is acid, it is neutralized with caustic and twenty times the weight of the Sn and Sb present added in excess, e.g., 2 grams potassium hydroxide in excess for every 0.1 gram of tin and antimony present in the solution. About ten times as much of tartaric acid is now added as the maximum weight of the two metals, followed by 30% hydrogen peroxide to oxidize the tin. The excess of peroxide is removed by boiling. To the slightly cooled solution a hot solution of pure oxalic acid is added, 5 grams of oxalic acid for each 0.1 gram of the mixed elements. CO_2+O_2 are evolved. The solution is boiled for about ten minutes and the volume made up to about 100 ml. Hydrogen sulfide is rapidly passed into the boiling solution until a change from a white turbidity to an orange color takes place and antimony begins to precipitate. The passage of the gas is continued for fifteen minutes, the solution diluted with hot water to a volume of 250 ml. and hydrogen sulfide passed into the boiling solution for another fifteen minutes. The flame is now removed and the H_2S "gassing" continued for ten minutes longer. The precipitated antimony pentasulfide is filtered off in a weighed Gooch crucible. It may be determined gravimetrically as Sb_2S_3, according to the procedure

[7] The original procedure may be found in Chem. News, Vol. XXI, p. 124.

given later, by washing with 1% oxalic acid and dilute acetic acid, by decantation, the solutions being hot and saturated with hydrogen sulfide. The precipitate washed into the crucible is dried in a current of CO_2 at 280 to 300° C. and weighed as Sb_2S_3.

Tin may be determined electrolytically in the filtrate evaporated to about 150 ml., the oxalic acid being nearly neutralized with ammonia. See Electrolytic Determination of Tin.

Antimony may be separated from tin in a hot hydrochloric acid solution by addition of pure iron. The iron and tin sulfides are dissolved in concentrated hydrochloric acid plus a few crystals of potassium chlorate. The solution should contain about 10% hydrochloric acid, more hydrochloric acid being added as the iron dissolves. Antimony is precipitated as metal.

Method 2. Arsenic, antimony and tin may be separated successively by distillation. For this purpose it is best to dissolve the sulfides in concentrated sulfuric acid, or to attack complex mixtures such as ores, slags, scums, alloys, etc. with nitric acid followed by sulfuric.[8] Prior to distillation the solution is evaporated to 4 ml. in a 150 ml. round-bottom flask with a 13–14 cm. neck which is 2.5 cm. wide. The flask is provided with a distilling head, dropping funnel, condenser and receiver (750 ml. flask containing 50–100 ml. water, as shown in Fig. 6). From 1 to 1.5 g. of hydrazine sulfate is added to the sulfuric acid solution and a few ml. of water, and the stopper and other accessories are connected as indicated in Fig. 6. 80 ml. of conc. hydrochloric acid are run in, and then 1 g. of borax in 3 ml. of water, followed by a little more of the acid. A small flame is used in the distillation and CO_2 is passed in at a slow bubbling rate. The volume of liquid in the distilling flask is never reduced to less than five times the volume of sulfuric acid that was present. About 80 ml. distill in 40 minutes. When it is expected that all of the arsenic has distilled, the receiver is changed and 20–30 ml. of conc. hydrochloric acid are added to the distilling flask. Finally a portion of the distillate is tested with methyl orange and 0.1 N $KBrO_3$ to prove that no more arsenic is being distilled. The arsenic may be determined in the combined distillates by any convenient volumetric or gravimetric procedure.

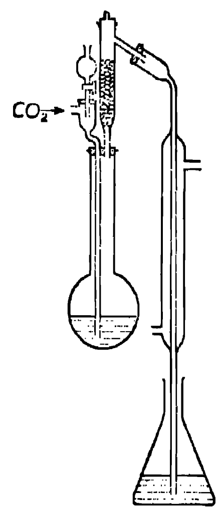


Fig. 6.—Apparatus for Separation of Arsenic, Antimony and Tin.

To remove antimony from the distilling head, let a little conc. HCl flow through, then put a stopper in the lower end of the head and allow conc. HCl to stand in contact with the glass fragments for 10 minutes; this acid is used in the distillation of the antimony chloride. Add 7 ml. of 85% phosphoric acid, sp. gr. 1.7, or double this amount if the tin percentage is high. Connect the flask with the condenser as indicated in Fig. 7. The receiver contains 50–100 ml. of water. Start adding conc. HCl after the temperature is 150° C. and distill at a rate of 1 drop per 1–2 seconds. The antimony distills in 40–50

[8] H. Biltz, Z. anal. Chem., 81, 82 (1930); 99, 1 (1934). See Plato, Z. Anorg. Chem., 68, 26 (1911); Z. Anal. Chem., 50, 641 (1911); Hartmann, Z. Anal. Chem., 58, 148 (1919). See also K. Röhre, Z. Anal. Chem., 65, 109 (1924).

minutes. Test with fresh receiver and treat some of the distillate with H_2S until no more antimony chloride distills. The tin is retained by the phosphoric acid. The antimony in the distillate may be determined gravimetrically or volumetrically.

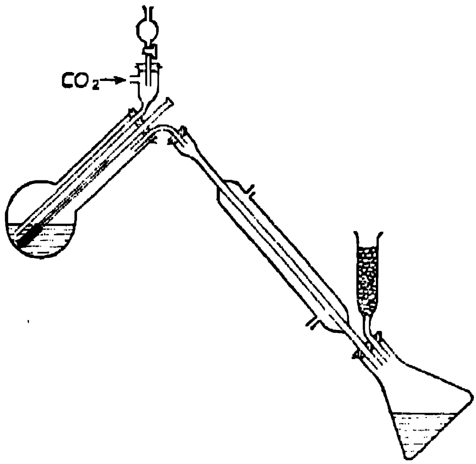


FIG. 7.—Apparatus for Separation of Antimony and Tin.

Distillation of Tin.—Mix 1 part of 40% HBr, sp. gr. 1.4, with 3 parts of conc. HCl and add to the distilling flask as in case of the antimony distillation, but keep the temperature at 140° C. or lower because bismuth is distilled at temperatures above 145°.

An all-glass apparatus suitable for the separation and determination of large or small quantities of arsenic, antimony and tin by the distillation method has been described by J. A. Scherrer.[9] The apparatus consists of a dropping bulb (50-ml.) for the acid connected through a stop-cock to an enlarged section provided with a side-arm tube for the introduction of CO_2, and thence by a 3–4 mm. tube to the bottom of the 200-ml. distillation flask which is provided with a thermometer well extending nearly to the bottom of the flask. The neck of the flask is 2–5 cm. in diameter; a side tube is sealed to a bulb-type condenser.

The solution is prepared by $HNO_3-H_2SO_4$ attack and all but 5 ml. of the latter are evaporated off; 30–40 ml. of sulfurous acid are added and the solution is evaporated to 10 ml. and transferred with 100 ml. of HCl to the distilling flask. The arsenic is distilled off at 111–112° C., until the residual volume is 50 ml. Then 25 ml. more of acid are added and the solution is distilled down to 50 ml. The receiver contains 50–100 ml. of water.

The receiver is changed and the antimony chloride is distilled in a CO_2 stream after 7 ml. of 55% H_3PO_4 has been added, until 75 ml. of HCl, added at the rate of 30–40 drops per minute, have been distilled over. The receiver is changed and 25 ml. more of the acid are added and distilled in the same manner. The temperature during distillation is 155–165° C.

[9] J. A. Scherrer, J. Res. Nat'l. Bureau of Stands., 16, 253 (1936).

The solution is cooled to 140° C., the receiver is changed and a mixture of HCl (3 parts) and HBr (1 part) is added at 30–40 drops per minute. After 50 ml. of the mixed acid have been distilled the receiver is changed and 25 ml. more of the mixed acid are added and distilled.

The arsenic, antimony and tin are determined by conventional procedures.

Separations in the Presence of Fluoride.—Trivalent antimony and arsenic, together with copper, lead, bismuth, and cadmium are separated from stannic tin in solutions that contain a moderate amount of hydrochloric or sulfuric acid together with 2–5 ml. of 48% hydrofluoric acid per 100–500 ml. by passing in hydrogen sulfide. Vessels of platinum, paraffin, glass coated with paraffin, baekelite, or other synthetic resins, or even glass may be used. (The latter only when one works rather rapidly; the filtrate must be stored in a more resistant vessel, or else treated with 4 g. of boric acid to bind the fluoride.)[10] These methods are excellent for the separation of the various elements from tin.[11]

Separation of Small Amounts of Antimony (together with P, Se, Te, V, Sn, W) from Molybdenum.—To the ammoniacal solution sufficient ferric iron solution is added to form the basic iron salts of the elements in question. Molybdenum remains in solution. Basic ferric antimonate (together with the elements mentioned above) remains in the precipitate.

Separation from Silicon.—Evaporate to fumes with sulfuric acid. Cool and dilute with ten volumes of water and filter from the insoluble SiO_2. Antimony passes into the filtrate.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF ANTIMONY

The accuracy and rapidity of volumetric methods for the determination of antimony leave little to be desired in the estimation of this element, so that the more tedious gravimetric methods are less frequently used. The following procedures are given in view of possible utility in certain analyses.

[10] McCay, "Separation of Antimony and Tin," J. Am. Chem. Soc., **31**, 373 (1908); "Separation of Tin and Arsenic," J. Am. Chem. Soc., **45**, 1187 (1923); "Separation Arsenic and Antimony," J. Am. Chem. Soc., **50**, 368 (1928); "Analysis of Tin-Antimony Alloys," J. Am. Chem. Soc., **32**, 1241 (1910).

[11] The tin may be determined by removing the fluoride by evaporation (platinum vessel), or by binding the fluoride with boric acid, after which the tin may be precipitated as stannic sulfide, or with cupferron, or deposited electrolytically. The last process is not complete for 1–2 mg. of tin usually fail to be deposited. Furman, Ind. Eng. Chem., **10**, 1071 (1923). Sand, Analyst, **59**, 335 (1934).

DETERMINATION OF ANTIMONY AS THE TRISULFIDE, Sb_2S_3[12]

Although hydrogen sulfide passed into a cold solution tends to precipitate Sb_2S_5, in hot strongly acid solutions the lower sulfide, Sb_2S_3, tends to form. The higher sulfide is decomposed at 230° C. with formation of Sb_2S_3 and the volatilization of sulfur. A temperature[13] of 280 to 300° C. is even more favorable for this transformation. The method takes advantage of these conditions for formation of antimony trisulfide, in which form it is weighed.

Procedure.—The solution of antimony, free from arsenic and elements precipitated by H_2S in acid solution, is treated in an Erlenmeyer flask with concentrated hydrochloric acid until the solution contains about 20% of the concentrated acid. The mixture is heated to 90 to 100° C. and a slow current of hydrogen sulfide is passed into the hot solution until the precipitate passes from a yellow color through an orange and finally becomes a dark red to black color. The flask is agitated gently to coagulate the precipitate, which settles in a crystalline form. The solution is diluted with an equal volume of water, washing down the walls of the flask. A slight turbidity is generally seen, due to precipitation of a small amount of antimony that remains in solution in a strong acid solution. H_2S is now passed into the diluted solution until it becomes clear; thirty-five to forty minutes are usually sufficient to precipitate all the antimony. The precipitate is transferred to a weighed Gooch crucible, washed with small portions of water containing hydrogen sulfide, and finally with pure water.

It is a common practice, at this juncture, to wash the precipitate with carbon disulfide or carbon tetrachloride to remove precipitated sulfur. Alcohol is now used, followed by ether, and the precipitate sucked dry.

The Gooch crucible is placed in a large combustion tube and heated in a current of dry, pure CO_2 at 130° C. for an hour. The temperature is now raised to 280 to 300° C. and the heating continued for two hours. The residue will consist of pure Sb_2S_3.

$$Sb_2S_3 \times 0.7169 = Sb, \qquad \text{or} \qquad Sb_2S_3 \times 0.8582 = Sb_2O_3.$$

NOTES.—Antimony may be determined by oxidation of the sulfide precipitate by means of fuming nitric acid. The mixture evaporated to dryness is ignited and the residue weighed as Sb_2O_4. The temperature of the ignition should be between 750 to 800° C. The volatile trioxide forms at a little above 950° C. The procedure requires greater care than the sulfide method and possesses no advantages.

Pure carbon dioxide may be obtained from limestone placed in a Kipp generator. The gas is dried by passing it through strong sulfuric acid. It should be free from oxygen of the air. It is advisable to sweep out the air from the generator before attaching it to the combustion train. The air in the tube is swept out with carbon dioxide before heating the sample.

Properties of Sb_2S_3: *m.w.*, 339.70; *sp.gr.*, 4.65; fusible and volatile; solubility, 0.000175 gram per 100 ml. H_2O; decomposed by hot H_2O; soluble in alkalies, NH_4HS, K_2S, conc. HCl.

DETERMINATION AS THE OXIDE, Sb_2O_4

The sulfide of antimony obtained as described in the first procedure is treated with ammonium hydroxide and hydrogen peroxide added in excess and

[12] Method of Vortmann and Metzel modified.
[13] Paul, Z. anal. Chem., 31, 540, 1892.

the solution evaporated in a weighed crucible to dryness, with the necessary precautions, and, after being moistened with concentrated sulfuric acid, ignited to expel the ammonium salts. The residue is weighed as Sb_2O_4.

ELECTROLYTIC DETERMINATION OF ANTIMONY[14]

The chief condition for the success of the electrolytic deposition of antimony in metallic form is the absence of polysulfides, since these substances prevent the element from being deposited, $2Sb+3Na_2S_2=2Na_3SbS_3$. The formation of polysulfides may be prevented during electrolysis by addition of potassium cyanide to the solution, $Na_2S_2+KCN=Na_2S+KCNS$.

The results of this method, according to F. Henz, are invariably too high by 1.5 to 2% of the total antimony present in the solution. The sample for analysis should contain not over 0.2 gram antimony.

Procedure.—Antimony precipitated as the sulfide is washed and then dissolved off the filter by pouring pure sodium sulfide solution (sp.gr. 1.14) over the precipitate, the solution being caught in a weighed platinum dish, with unpolished inner surface. The total volume of the solution should be not over 80 ml. (if less than this, additional Na_2S solution is added to make up to 80 ml.). Sixty ml. of water followed by 2 to 3 grams of potassium cyanide (C. P.) are added and the cyanide dissolved by stirring with the rotating anode. The solution heated to 60 to 70° C. is electrolyzed with a current of 1 to 1.5 amperes, E.M.F.=2 to 3 volts. Two hours are generally sufficient to deposit all the antimony. The light-gray deposit adheres firmly upon the cathode. The deposition is better if the cathode is roughened by means of a sand blast. With an amperage of 0.2 a longer period of 12 to 15 hours will be required for complete deposition. Without breaking the current the solution is siphoned off, while fresh water is being added, until the current ceases to flow through the liquid. The cathode is washed thoroughly with water, followed by alcohol and ether, and then dried at about 80° C., cooled in a desiccator and weighed.

The antimony deposits may be removed by heating with a solution of alkali polysulfide or by a mixture of equal parts of saturated solution of tartaric acid and nitric acid.

[14] Method first proposed by Parrodi and Mascazzini, Z. anal. Chem., **18**, 587, 1879, modified by Luckow, Z. anal. Chem., **19**, 13, 1880, and later improved by Classen and Reiss, Berichte, **14**, 1629, 1881; **17**, 2474, 1884; **18**, 408, 1885; **27**, 2074, 1894.

F. Henz, Z. anorg. Chem., **37**, 31, 1903.

VOLUMETRIC METHODS

POTASSIUM BROMATE METHOD FOR DETERMINING ANTIMONY[15]

Outline.—This method is of special value in determining antimony in hard lead and alloys. It was first suggested by Györy and later modified by Siedler, Nissensen and Rowell.[16] The process is based upon the oxidation of antimony from the trivalent to the pentavalent form by potassium bromate, the following reaction taking place:

$$KBrO_3+3SbCl_3+6HCl=3SbCl_5+KBr+3H_2O.$$

Standard Solutions.

Antimony Chloride Solution.—Six grams of the C. P. pulverized metal are dissolved in 500 ml. of concentrated hydrochloric acid together with 100 ml. saturated bromine solution, more acid and bromine added if necessary to effect solution. After expelling the bromine by boiling, about 200 ml. concentrated hydrochloric acid are added and the whole made up to 1 liter. Fifty ml. =0.3 gram antimony.

N/10 Potassium Bromate Solution.—2.7835 grams of analytical reagent salt, recrystallized and dried at 150° C., are dissolved in water and made up to 1 liter. The solution may be standardized against pure antimony or arsenious oxide. One ml. of N/10 $KBrO_3$ =0.006088 gram Sb.

Methyl Orange.—0.1 gram M. O. per 100 ml. of distilled water. The indicator should be free from sediment.

Saturated Bromine Solution.—500 ml. concentrated hydrochloric acid saturated with 70 ml. of bromine.

Procedure. ***Solution.***—One gram of the finely divided alloy is brushed into a 500-ml. beaker, 100 ml. of concentrated hydrochloric acid and 20 ml. of saturated bromine solution are added. The beaker is covered and placed on the steam bath until the metal dissolves. It may be necessary to add more bromine and acid to effect complete solution. In case the oxides of antimony and tin separate out and do not redissolve, fusion with sodium hydroxide may be necessary. Bromine is now expelled by boiling the solution down to about 40 ml.

Reduction.—One hundred ml. of concentrated hydrochloric acid and 10 ml. of a fresh saturated solution of Na_2SO_3 are added and the solution boiled down to 40 ml., on a sand bath, to expel arsenic and the excess of normal sodium sulfite. Samples high in arsenic may require a repetition of the reduction.

Titration.—The cover and sides of the beaker are rinsed down with 20 ml. of hydrochloric acid (sp.gr. 1.2) followed by a few ml. of hot water and the solution heated to boiling on a sand bath. The standard bromate solution is now run into the hot solution of antimony to within 2 to 3 ml. of the end-point, this having been determined in a preliminary run with methyl orange added in the beginning, 4 drops of methyl orange are added and the titration completed cautiously until the color of the indicator is destroyed. If iron

[15] S. Györy, Z. anal. Chem., **32**, 415, 1893. J. B. Duncan, Chem. News, **95**, 49, 1907.
[16] H. W. Rowell, J. Soc. Chem. Ind., **25**, 1181 (1907).

or copper is present the final product will appear yellow. Since the end-reaction is slow the last portion of the reagent should be added drop by drop with constant stirring.

1 ml. N/10 $KBrO_3$ = 0.006088 gram Sb.

NOTES.—Since antimony chloride begins to volatilize at 110° C. and boils at 223° C. it is advisable not to carry the concentration too far while expelling arsenic.

Lead, zinc, tin, silver, chromium, and sulfuric acid have no effect upon the determination, but large quantities of calcium, magnesium, and ammonium salts tend to make the results high. Low [17] found that copper produced high results, approximately .012% too high for every 0.1% of copper present. With larger amounts of copper, the end-point became difficult to detect owing to the depth of the yellow color, so that in case of brass and copper alloys, the method must be modified by a procedure for removal of the copper. Lead up to 95% caused no difficulty. Iron, in amounts such as are commonly met in alloys of lead, does not interfere.

During the course of analysis antimony may be isolated as the sulfide; this is dissolved in concentrated hydrochloric acid, and reduced and concentrated to expel arsenic that may be present as a contamination, and the resulting solution titrated with potassium bromate as directed above.

Sources of Error. (*a*) Imperfect volatilization of arsenic. (*b*) Incomplete expulsion of SO_2. (*c*) Over-titration if insufficient hydrochloric acid is present.

No loss of antimony occurs at temperatures below 108° C.

POTASSIUM IODIDE METHOD FOR DETERMINING ANTIMONY

Procedure.—To 1 gram of fine sawings or filings in a 16-oz. Erlenmeyer flask add 60 ml. of concentrated hydrochloric acid and heat on an asbestos board or on the water bath just below boiling. When hydrogen is no longer evolved, decant the liquor and wash twice with concentrated hydrochloric acid, retaining the antimony in the flask. Now dissolve the antimony by adding 15 ml. of concentrated hydrochloric acid and solid potassium chlorate, a few crystals at a time, until the antimony is in solution, the liquid being kept hot. Expel chlorine by boiling, add 50 ml. of concentrated hydrochloric acid and again bring to boiling. Cool and add 20 ml. of 20% potassium iodide solution and 1 ml. of carbon disulfide or tetrachloride. Titrate the liberated iodine with tenth-normal sodium thiosulfate. The brown color will gradually disappear from the solution and the last traces of free iodine will be collected in carbon disulfide or carbon tetrachloride, giving a pink color. When this pink color disappears the end-point has been reached.

One ml. N/10 $Na_2S_2O_3$ = 0.006088 gram Sb.

$Na_2S_2O_3$ is standardized against .3 gram antimony as in case of Potassium Bromate Method, the above procedure, however, being followed. Antimony must be free from copper and arsenic.

NOTES.—The following reversible reaction is of interest: "R" representing a trivalent metal with oxidation to pentavalent form.

$$R_2O_3 + 2I_2 + 2H_2O = R_2O_5 + 4HI.$$

The reaction goes to the right when an alkali is present to neutralize the free acid formed; e.g., Mohr's process for determining arsenic by titration of the lower oxide with iodine in presence of sodium bicarbonate. The reaction goes to the left in presence of strong acid; e.g., Weller's process for the determination of antimony in an acid solution.

[17] A. H. Low, "Technical Methods of Ore Analysis."

The solution should not contain more than $\frac{1}{5}$ of its volume of hydrochloric acid (sp.gr. 1.16), since too much hydrochloric acid gives high results, owing to the action of hydrochloric acid on potassium iodide. Too little acid leads to the separation of basic iodides and chlorides of antimony. The solution is best boiled down to 20% hydrochloric acid (above strength).

Stannous chloride may be used in place of thio-sulfate in titration of iodine.

$$SbCl_5+2KI=SbCl_3+2KCl+I_2 \quad \text{and} \quad I_2+SnCl_2+2HCl=SnCl_4+2HI.$$

DETERMINATION OF ANTIMONY BY OXIDATION WITH IODINE

The procedure originated by Mohr and modified by Clark depends upon the reaction $Sb_2O_3+2I_2+2H_2O=Sb_2O_5+4HI$.

The reaction takes place when iodine is added to a solution of antimonous salt in presence of an excess of alkali bicarbonate. In an acid solution oxidation with iodine does not go beyond Sb_2O_3.

Procedure. ***Solution.***—The sample is brought into solution by one of the procedures given under "Preparation and Solution of the Sample." Alloys of antimony, lead, and tin are treated according to directions given for this combination.

Titration.—To the hydrochloric acid solution of antimony is added tartaric acid or Rochelle salts, the excess of the acid neutralized with sodium carbonate, the solution made barely acid with hydrochloric acid and a saturated solution of sodium bicarbonate added in the proportion of 10 ml. bicarbonate solution for each 0.1 gram of Sb_2O_3. Starch is added as an indicator and the solution titrated with N/10 iodine.

1 ml. N/10 iodine = 0.006088 gram Sb.

NOTE.—The titration should be made immediately upon addition of the sodium salts. Addition of the starch as the end point is approached will result in a more intense blue color.

PERMANGANATE METHOD

Antimonous salts may be titrated with standard potassium permanganate. The iron value for the permanganate multiplied by 1.075, or the oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) value multiplied by 0.9532, will give the antimony value.

DETERMINATION OF ANTIMONY IN BRASS- PERMANGANATE METHOD

Reagents. ***Potassium Permanganate.***—0.3 g. of $KMnO_4$ is dissolved in water and made to 1000 ml. The reagent is standardized against 25 mg. of pure antimony that has been dissolved in 15 ml. of boiling sulfuric acid and treated as described in the procedure below, under 4 and 5.

Procedure.—1. A sample of 5 grams of brass is dissolved in a 250-ml. beaker in 25 ml. of concentrated nitric acid (d. 1.42). After the action has ceased the solution is boiled to expel the oxides of nitrogen. Now 125 ml. of boiling water are added and the solution allowed to settle for an hour or more, keeping the temperature just below boiling. The tin and antimony precipitates are filtered on double 9 cm. closely woven filter papers, keeping the solution hot, and then washed with boiling water. The filtrate is discarded.

2. The papers and residue, transferred to a 400-ml. beaker, are treated with 25 ml. of concentrated nitric acid (d. 1.42), 5 grams of ammonium persulfate,

and 15 ml. of concentrated sulfuric acid (d. 1.84) and boiled down to strong fumes. (The reaction may be conveniently carried out in a "copper flask" of pyrex glass.) If the solution is brown, 5 ml. of concentrated nitric acid are added to the cooled solution and about 1 gram additional of persulfate and the boiling to fumes repeated.

3. When the solution is colorless, it is cooled, 20 ml. of water added, together with 20 ml. concentrated hydrochloric acid (d. 1.20) and (cautiously) 1 gram of sodium sulfite and the SO_2 completely expelled by gentle heating for 10 minutes, or longer.

4. The solution is diluted with 200 ml. of water, and cooled under running water to 10° to 12° C., then titrated with the standard potassium permanganate solution to a decided pink color.

NOTES.—Antimony is precipitated quantitatively with meta-stannic acid in alloys containing a large amount of tin.

The filter paper is destroyed by ammonium persulfate and nitric acid, while tin and antimony go into solution with the sulfuric acid. Fuming nitric and sulfuric acids may be used, in place of the persulfate and nitric acid, but are not so efficient.

The solution is kept hot to prevent solution of the meta-stannic acid.

Arsenic in the alloy necessitates a correction.

In case of alloys containing considerable amounts of tin and antimony, smaller samples should be taken and stronger potassium permanganate solution than is recommended for brass.

Should the oxides remain undissolved upon fuming with sulfuric acid, a small piece of filter paper added ($\frac{1}{8}$ inch square) will effect reduction and solution of the oxides. The solution should be heated until the carbon of the filter is destroyed and the solution clears and becomes colorless.

Acidity with HCl—10 to 20 per cent by volume of concentrated HCl—is permissible.

INDIRECT EVOLUTION METHOD

The method depends upon the evolution of H_2S from the sulfide of antimony decomposed by concentrated hydrochloric acid, the amount of hydrogen sulfide being the same for either Sb_2S_3 or Sb_2S_5, the following reactions taking place. Other sulfides must be absent.

1. $Sb_2S_3+6HCl=2SbCl_3+3H_2S$.
2. $Sb_2S_5+6HCl=2SbCl_3+2S+3H_2S$.

The details of the method are practically the same as determination of sulfur by the evolution method in the analysis of iron and steel. See chapter on Sulfur. The antimony sulfide precipitate is placed in the evolution flask, concentrated hydrochloric acid added with an equal volume of water and the evolved hydrogen sulfide absorbed in an ammoniacal solution of cadmium chloride. The precipitated cadmium sulfide is then titrated with iodine in an acid solution.

One ml. N/10 I = 0.001603 gram S, since 3S = 2Sb, therefore Sb = S × 2.532, hence, 1 ml. N/10 I = 0.004059 gram Sb.

Analysis of Stibnite.—The method worked out by McNabb and Wagner [18] makes use of the evolution method for determination of sulfide sulfur with

[18] Wallace M. McNabb and E. G. Wagner, Ind. Eng. Chem., Anal. Ed. 1, 32, 1929; *ibid.*, 2, 251, 1930.

additional provision for free and sulfate sulfur, which the mineral is apt to contain. Antimony is determined in the hydrochloric acid solution of antimony that remains in the evolution flask. A simple apparatus, made up of apparatus commonly found in an analytical laboratory, may be used. Carbon dioxide gas passed through assists in the complete sweeping out of H_2S into the cadmium chloride solution. Illustration of the apparatus and details of the analysis may be found in the original articles of these authors in the references given.

Other Methods.—Antimony may be reduced to the trivalent condition by shaking its solution with mercury.[19] This method may be applied to the solutions which contain arsenic and stannic acids as well as cadmium and bismuth in hydrochloric acid solution. Cupric salts are reduced to cuprous, but the latter are selectively reoxidized if air is bubbled through the solution for fifteen to twenty minutes.

Procedure.—Place the solution acidified with about one-sixth of its volume of conc. hydrochloric acid in a glass bottle provided with a well-ground stopper and of capacity 150 to 250 ml. Add 20 to 25 ml. of pure mercury. Displace the air in the bottle with carbon dioxide. The bottle is then shaken five minutes by hand or by machine, in ordinary cases. If, however, the antimony is in the form of pyroantimonate a period of one hour is necessary for the reduction with vigorous shaking. After reduction the solution is decanted through a filter and the reductor is washed free of antimony with 1 to 9 hydrochloric acid. If copper is present, the filtrate and washings must be treated with a rapid current of air. If the amount of copper is from .02 to .06 grams, the results for antimony will be 0.3 to 0.5 mg. too low. Otherwise, the method gives practically perfect results.

If antimony and arsenic are present in a mixture their sum may be determined by titration with bromate, and afterwards the antimony may be selectively reduced as described. Any one of the oxidizing agents potassium, bromate, iodate or ceric sulfate may be used in the titration of the antimony.[20]

DETERMINATION OF SMALL AMOUNTS OF ANTIMONY

Details of this procedure were worked out by Mr. W. Shelton, under the direction of Mr. W. C. Ferguson, chief chemist, and Mr. E. Fitzpatrick, first assistant chemist, Nichols Copper Company. The method is accurate and is of special value in determining traces of antimony in copper and in alloys.

[19] McCay, Ind. Eng. Chem., Anal. Ed. 5, 1, 1933.

[20] The titration with ceric sulfate is selective for antimony in the presence of minor proportions of arsenic. The solution should contain 15% by volume of concentrated hydrochloric acid. The end point is determined by the bleaching of a drop of 0.1% methylorange solution. Cf. Rathsburg, Ber., **61**, 1663 (1928); Furman, J. Am. Chem. Soc., **54**, 4235 (1932).

Since arsenic may also be determined a separation by distillation is necessary if the latter is present.

Description of Generator

The generator consists of three separate parts:

1. Glass cap which is placed over funnel *A*, to hold the disc of test paper in place.
2. *F–G*, this part of the apparatus has two small parts: *F*, which is a tube of glass $\frac{13}{16}''$ long, $\frac{1}{16}''$ wide, fitted into a rubber tube *G* $\frac{5}{16}''$ wide, which in turn is fitted into the lower part of funnel *A*. The part *F* is a very important one and care should be taken to have exactly the same size glass tubing and that distance from the top of *A* to top of *F* is $\frac{5}{16}''$.

The entire apparatus consists of parts *A*, *B*, *C*, *D*, *E*, *F*, *G*.

A. The funnel for test paper.

B. Bulb for holding cotton saturated with lead acetate to absorb any H_2S gas should any be present when generator is operating. Use 0.5 gms. of cotton.

C. This part extends to *E*, which has two purposes: No. 1. For introducing acid, H_2O, the test, etc., without opening the apparatus. No. 2. As a safety valve, should the apparatus become clogged or stopped up the pressure will exert itself in this direction.

D. Upper part acts as condenser. The lower part is ground to fit the bottle No. 3.

E. This part is explained in *C*.

3. This part is the bottle which has 250-ml. capacity with a ground mouth to receive the No. 2 part of generator.

NOTE: All generators must be made and assembled as nearly uniform as possible to assure concordant results.

4. This figure shows the manner in which the test is placed on funnel *A*, and how the cap fits over and holds the test paper in position. See Fig. 8.

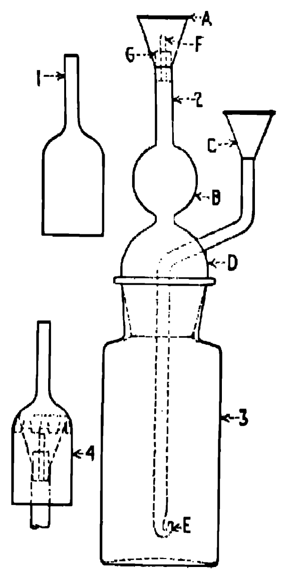


FIG. 8.—Fitzpatrick Apparatus for Determining Traces of Antimony.

Chemicals and Solutions

All chemicals and solutions must be previously tested for arsenic and antimony before using.

HCl—C.P. Conc. redistilled, As and Sb free.
HNO_3—C.P. Conc.
NH_4OH—C.P. Conc.
$Fe(NO_3)_3$—5 lbs. to 9 liters, about 3% solution.
$KClO_3$—Use dry crystals.
$FeCl_2$—2 lbs. to 2 liters.
$ZnCl_2$—20 lbs. to 9 liters HCl (purified by dissolving 15 g. zinc in 500 ml. of the above stock solution).
Zinc Shot—Wash in dilute HCl before using.
$SnCl_2$ solution—52.5 g. per liter.
5% $HgCl_2$ used for test paper. 5 g. to 100 ml. H_2O. (Cut with die into circles of $1\frac{5}{8}''$ in diameter.)
10% Pb $(C_2H_3O_2)_2$ for cotton. 10 g. to 100 ml. H_2O.
5% NH_4OH_2 for developer of test paper, 200 ml. NH_4OH per liter.
1% $AuCl_3$ solution.

Preparation of Test Paper.—The paper used must be selected, when purchased, for evenness of thickness and texture in sheets of 24″×40″.

The above sheets are cut in half and saturated with a 5% $HgCl_2$ solution—the wet sheet is then placed on a glass plate and the surplus solution is squeezed out with a 10″ rubber roller, which is rolled over the paper twice. Care must be exercised to roll the paper evenly and with good pressure using the same conditions for each sheet. The sheet is now hung over a line to dry, in a warm place away from the sunlight or any influence of hydrogen sulfide. Do not dry paper in oven. When dry the paper is cut with die into pieces of $1\frac{5}{8}''$ in diameter. Keep the discs of test paper in a dark-brown bottle and away from the light until used.

Enough test paper should be made at one time to last for about 3 months.

Each new lot made should be tested with known amounts of As and Sb and compared with standards, before using. Should they not check close it is advisable to make new set of standards from the test paper just made.

Preparation of Lead Acetate Cotton.—A roll of absorbent cotton is opened and saturated with a 10% solution of lead acetate and surplus drained off, then hung on a line to dry in a warm place away from the influence of hydrogen sulfide. Do not dry in oven. When dry, place in stoppered bottle until used.

Precautions

Blank.—A blank test should be run with each day's work, using all the reagents used in actual tests.

The stain obtained on test paper from blank is subtracted from the actual test.

Limits.—The limits of As or Sb that can be determined by this method must be within the following figures:

As separately from .00002 g. to .00010 g.
Sb separately from .00002 g. to .00015 g.

Checks..—A 10 g. sample of standard copper known to be free from As or Sb is weighed out and known amounts of As and Sb are introduced.

Distillation.—The distilling apparatus should *not* be used for any other tests when the As or Sb is known to be higher than the limits for this work.

Zinc.—The zinc shot must be cleaned with dilute HCl and washed with distilled water each day to insure proper action in generator, and to expel any sulfide present which would spoil the test.

Generator.—The presence of nitrates, chlorates, or compounds of copper interferes with generation of arsine and stibine, so care must be exercised to have these compounds eliminated.

Large quantities of ferrous and ferric compounds interfere also in the generation of stibine to some degree. The small amount of Fe that gets into the test from the process of distillation is overcome by the addition of 2 ml. stannous chloride—at times more may be required.

Uniformity.—Uniformity must be strictly adhered to throughout the test.

In the determination of antimony in presence of arsenic the removal of the latter is necessary. This is accomplished by distillation of $AsCl_3$ according to the procedure outlined in the chapter on arsenic.

Standard Antimony Solution and Standard Stains

Antimony Solution.—A stock solution is made up by weighing out 0.553 g. $KSbO_3C_4H_4O_6$, which is dissolved in distilled water and made up to 2000 ml., which represents 1 ml. = .0001 g. Sb.

From the above stock solution take 100 ml. and make up to 1000 ml. This solution now equals 1 ml. = .00001 g. Sb, which is used for making the standard stains and introducing into checks.

OUTLINE OF THE METHOD

Preparation of Standard Stains.—Extreme care must be taken when preparing the standard stains.

Wash the generator thoroughly with distilled water, place freshly prepared lead acetate cotton in the bulb, *B*, No. 2, and see that the top of part *F*, No. 2, is exactly $\frac{5}{16}''$ from the top of part *A*, No. 2.

Now introduce into bottle of generator, No. 3, the required amount of As or Sb as desired and then add 50 ml. redistilled HCl, As free, 2 ml. stannous chloride solution and make up to 220 ml. with distilled water.

The disc of mercuric chloride test paper is now placed on top of funnel *A*, No. 2, and the glass cap, No. 1, is forced over the paper holding it in place.

Now introduce 15 g. metallic zinc shot and place the No. 2 section with No. 1 attached into the No. 3 or bottle of generator. The apparatus now being assembled, observe that the apparatus is fitted together tightly, because as soon as the zinc is introduced, arsine and stibine are generated immediately. Place the generator into the water bath to maintain constant temperature, which should be about 70° F. Allow the generator to operate for 1 hour.

The glass cap, No. 1, is now removed and the test paper is developed in a No. 2 beaker with 5% NH_4OH solution for three minutes, then washed 5 times with distilled water. The test paper is now toned with a 1% $AuCl_3$ solution by allowing the test paper to remain in solution for five minutes. The test paper will now have a violet or purple stain, the intensity depending on the amount of As or Sb introduced. Wash the paper 5 times with distilled water and preserve in 50 ml. glass stoppered bottles containing about 5 ml. water. Keep bottles in dark place, because the stains darken on exposure to light.

Duplicate tests are made, finally selecting of two the one which is the most uniform.

The stains are made to represent the following amounts:

	Sb
1	.00002
2	.00004
3	.00006
4	.00008
5	.00010
6	.00012
7	.00014
8	.00016

Procedure for Refined Copper

A blank is run with all tests.

Weigh 10 g. of the shot or drilled sample into a No. 3 beaker. Add 50 ml. conc. HNO_3, C.P. As free, let stand covered with watch glass until the action has subsided. Now place beaker on wire gauze over Bunsen flame and heat until all the copper is dissolved.

Remove from flame, dilute to 150 ml. with distilled water (if too basic add a few drops of HCl to clear the solution). Add 2 ml. ferric nitrate solution, stir, then make ammoniacal by adding C.P. ammonium hydrate (As free). Bring to boiling. Remove from flame and filter through a 15 cm. fluted Perfection filter paper. Immediately wash the filter paper free from copper compounds with hot water, using dilute ammonia where necessary to wash out any copper salts that have crystallized.

The precipitate (which contains both As and Sb) is dissolved off the filter with hot dilute hydrochloric acid, by means of a wash bottle, into a No. 4 casserole. Wash the filter three times with hot water.

Add a pinch of $KClO_3$ to the casserole, cover with watch glass, place the casserole in an asbestos cut out over Bunsen burner and boil the contents down to 10 ml., taking care that it does not roast on the sides.

Distillation.—Transfer the contents of the casserole to the distilling apparatus. Add 20 ml. ferrous chloride and 20 ml. zinc chloride solution, and distill until the contents of flask begin to froth. Now add, drop at a time, 35 ml.

HCl, through the dropping funnel which is connected to flask. Distill until all the HCl is out of the funnel and out of the flask.

The distillate is received in a No. 4 beaker having 40 ml. H_2O in which both the As and Sb are contained.

The above distillate is now transferred and washed from the beaker into the special designed generator. Add 2 ml. stannous chloride, which insures a complete reduction of any ferric compounds present. Dilute the contents of generator to 220 ml. Place disc of $HgCl_2$ test paper on the funnel top, then put on cap to hold in place. Add 15 g. metallic zinc or 1 No. 6 porcelain spoonful. Take care that the generating apparatus is properly closed, then place into water bath to maintain constant temperature, which should be about 70° F. The apparatus is allowed to operate for one hour during which time the arsine and stibine generated shall affect the $HgCl_2$ test paper, causing a yellow or orange colored spot which varies in color and size according to the amount of As and Sb present. The paper is now removed from the apparatus and developed in a No. 2 beaker containing 5% ammonium hydrate solution for three minutes. The color of the spot now changes to a brownish black. Wash test paper five times with distilled water. Now cover the test paper with 10 ml. of 1% gold chloride solution, which tones the color of the spot to a violet or purple hue that fixes it so comparison can be made with the standard stains or spots to determine the amount of arsenic or antimony in the sample.

INDUSTRIAL PRODUCTS AND RAW MATERIALS

DETERMINATION OF ANTIMONY IN TARTAR EMETIC

Iodine in the presence of sodium bicarbonate oxidizes trivalent antimony to the pentavalent form as shown by the reaction:

$$K(SbO)C_4H_4O_6+6NaHCO_3+I_2 \\ =Na_3SbO_4+KNaC_4H_4O_6+2NaI+3H_2O+6CO_2.$$

Procedure.—10 grams of tartar emetic are dissolved in water, the solution diluted to 500 ml. and 20 ml. taken for analysis. This is diluted to 100 ml., 25 ml. of 2% sodium bicarbonate are added and the mixture titrated with N/10 iodine reagent.

$$1 \text{ ml. } N/10\ I = 0.016697 \text{ g. } K(SbO)C_4H_4O_6\cdot\tfrac{1}{2}H_2O.$$

Antimony in Rubber Goods.[21]—Three grams of the finely rasped rubber are treated in a Kjeldahl flask with 40 to 45 ml. of concentrated sulfuric acid.

[21] W. Schmitz, Chem. Zentralbl., ii, 1710, 1911. Analyst, 1912, p. 64.

A small quantity of mercury or mercury salt is added, together with a small piece of paraffin wax. The mixture is heated until the rubber is dissolved and the black liquid begins to clear. Two to 4 grams of potassium sulfate are then added and the heating continued until a colorless or pale yellow liquid is obtained. After cooling, 1 to 2 grams of potassium metabisulfite are added and an excess of tartaric acid. The liquid is diluted sufficiently to prevent the charring of the tartaric acid and boiled until the odor of sulfurous acid has disappeared. A few ml. of dilute hydrochloric acid are added, the liquid diluted to 200 ml., filtered through a dry filter, and 195 ml. titrated either with iodine or with potassium bromate (the latter in acid solution), as described under the volumetric procedures. Consult chapter on the analysis of rubber in volume 2.

DETERMINATION OF ANTIMONY IN SULFURIC ACID

The determination is made on a sample of 100 ml. This is diluted with water and the greater part of the acid neutralized with ammonium hydroxide (1 : 1). About two grams of copper sulfate are added and the sulfides precipitated by saturating the solution with H_2S. The sulfides are filtered off and antimony sulfide separated from CuS by extraction with $NaOH–Na_2S$ solution. Antimony is now determined in the extract. If the electrolytic method is to be used the polysulfides must be destroyed by oxidation with hydrogen peroxide, before electrolysis of the solution.

ANTIMONY IN SOLDER METAL AND ALLOYS WITH TIN AND LEAD[22]

Procedure.—Dissolve 2 grams of the sample of alloy in concentrated hydrochloric acid. When the metal is all in solution, add crystals of iodine until the solution is thoroughly permeated. The color at this point should be a deep purple. Boil until all of the iodine fumes have been driven out. The metallic antimony which did not go into solution in the hydrochloric acid should now be all dissolved. If it is not, add more iodine until the solution is complete. When all is in solution and the color changes to a straw yellow, cool, add a few ml. of starch solution. If a blue color appears, due to an excess of iodine, run in N/10 sodium thiosulfate solution until colorless. In case there is no blue color developed, add N/10 iodine until a faint blue appears. Now add 50 ml. of a saturated solution of Rochelle salts. Make alkaline to litmus by adding 25% sodium hydrate solution. Then make slightly acid with HCl

[22] Method communicated to author by Mr. B. S. Clark.

and finally alkaline with sodium bicarbonate. Cool and titrate with N/10 iodine.

NOTE.—"The method gives very good results. I have checked it up when there was one-tenth of a gram known antimony present and the results were within a reasonable limit of accuracy." [23]

DETERMINATION OF ANTIMONY IN A WHITE METAL ALLOY

SOLUTIONS REQUIRED

Mixed Acid.—Dissolve 20 g. of KCl in 500 ml of water, add 400 ml. of HCl (sp.gr. 1.18); mix and add 100 ml. of HNO_3 (sp.gr. 1.42).

Potassium Sulfide Solution.—Dissolve 140 g. of KOH in 800 ml. of distilled water and pass H_2S for two hours in the cold. Dilute to 2000 ml. with cold distilled water, mix and allow to stand overnight. Filter portions as required for use.

Potassium Hydroxide Solution.—Dissolve 100 g. of KOH in 500 ml. of water.

Potassium Iodide Solution.—20 g. of KI to 100 ml. of water.

Sodium Thiosulfate Solution.—Dissolve 24.8 g. of $Na_2S_2O_3 \cdot 5H_2O$ in 1000 ml. of water free from CO_2 and allow to stand 24 hours. Standardize by weighing out struck weights of approximately 0.3 g. of pure resublimed iodine, and brush into a covered 100 ml. beaker in which 2 g. of KI has been dissolved in 5 ml. of water; allow to digest in the cold a few minutes, dilute to a volume of 50 ml., titrate with the standard $Na_2S_2O_3$ solution to a pale straw color, add 2 ml. of starch solution and continue the titration to the disappearance of the blue color. The method of computing the strength of the $Na_2S_2O_3$ solution in terms of antimony is best shown by means of the following example:

Let A ml. of $Na_2S_2O_3$ solution be required to titrate B g. of iodine.

$$\text{Then 1 ml. } Na_2S_2O_3 \text{ solution} = \frac{B}{A} \text{ g. of iodine}$$

$$= \frac{B}{A} \times \frac{60.88}{126.92} \text{ g. of antimony.}$$

Also, standardize the $Na_2S_2O_3$ solution by running a sample of known antimony content, as described below.

[23] Standard method of the National Lead Company.

METHOD I[24]

Weigh out from 1 to 2 g. of the sawings,[25] brush into a 250 ml. beaker, add 100 ml. of the "mixed acid" solution, cover with a watch glass and heat on the hot plate until completely dissolved. When the metal is in solution, partly remove the covered glass, evaporate to a volume of 40 ml., cool, and allow to remain in the cold overnight. Decant the clear solution into a 600-ml. beaker, washing the residue of $PbCl_2$ three or four times by decantation with cold dilute HCl (1 : 1). Evaporate to near dryness, make just alkaline with KOH solution as shown by introducing a piece of litmus paper, add 12 g. of oxalic acid, dilute to a volume of 400 ml., boil, and pass H_2S through the hot solution for 45 minutes, keeping the solution hot [26] during the passage of the H_2S. Filter at once and wash the precipitate with a hot dilute solution of oxalic acid saturated with H_2S. Discard the filtrate.

Wash the precipitate from the filter paper back into the beaker with the least amount of water, add [27] 10 ml. of KOH solution and 10 ml. of potassium hydrosulfide solution, and digest on the water bath until the remaining residue is distinctly black.[28] Filter through the same paper into a 500-ml. Erlenmeyer flask, and wash the precipitate with hot water containing a little of the potassium hydrosulfide solution. Discard the residue.

Boil the filtrate down to a volume of 80 ml., carefully [29] add 100 ml. of HCl (sp.gr. 1.18) to the hot solution, boil down to a volume of 100 ml.[30] Cool, add about 1 g. of $KClO_3$, a pinch at a time, wash down the flask with about 20 ml. of HCl (sp.gr. 1.18) to remove any adhering $KClO_3$, and about 50 ml. of distilled water and boil down to a volume of 100 ml. Cool, add 5 ml. of the KI solution and titrate with standard $Na_2S_2O_3$ solution to a pale straw color. Decant into a clean flask to remove any separated sulfur,[31] add 1 ml. of CS_2 and continue the titration with standard sodium thiosulfate solution to the disappearance of a pink color in the CS_2.[32]

Accuracy.—Duplicate titrations should not disagree more than 0.1 ml.

RAPID METHOD FOR CONTROL WORK[33]

SOLUTIONS REQUIRED

Standard Potassium Permanganate Solution.—Dissolve 3.16 g. of $KMnO_4$ in about 500 ml. of distilled water and allow to stand several days. Filter

[24] G. W. Thompson Method modified. See A.S.T.M. Standards, 1927, p. 691.

[25] Pass a magnet through sawings to remove iron from saw.

[26] Add small amounts of water from time to time to keep the volume constant.

[27] In adding the alkaline solutions, it is preferable to pour them through the filter, in which case they should be hot and diluted with an equal quantity of water.

[28] It is good practice to fold a half filter, moisten it with the solution in the beaker, and work it around the sides to loosen and dissolve adhering sulfide.

[29] If added too fast the precipitate of antimony sulfide that is first formed will froth over the top of the flask.

[30] If the arsenic content be over 0.5 per cent it may not be completely expelled at this stage, in which case add 100 ml. HCl (sp.gr. 1.18) and 2 or 3 g. of $Na_2S_2O_3$ and boil down as before. Proceed as above described.

[31] If appreciable sulfur is present when the CS_2 is subsequently added, it will dissolve in the CS_2 and impair the delicacy of the end-point.

[32] Agitate well between each addition of the standard.

[33] Demorest Method modified. See J. Ind. and Eng. Chem., 5, 842 (1913).

through glass wool into a 1000-ml. graduated flask without washing, make up to the mark and mix. Standardize against Bureau of Standards sodium oxalate by accurately weighing out 0.2–0.3 g. of $Na_2C_2O_4$, brush into a 300-ml. beaker, dissolve with 200 ml. of hot distilled water, add 20 ml. of H_2SO_4 (1 : 1) and titrate with $KMnO_4$ solution to the first tinge of a permanent pink. Calculate[34] to antimony. Each ml. of the $KMnO_4$ solution should be equivalent to approximately 0.006 g. of antimony. Also standardize against a white metal alloy of known antimony content following closely the conditions as specified for the analysis of the sample.

Method

Weigh from 1 to 2 g. of the sawings into a 300-ml. Kjeldahl flask, add 15 ml. of H_2SO_4 (sp.gr. 1.84) and heat on gauze over a Bunsen flame until completely decomposed.[35] Cool, add 100 ml. of cold distilled water and 15 ml. of HCl (sp.gr. 1.18) and boil for five minutes. Add 100 ml. of cold distilled water, cool by immersing in running tap water and, when cold, titrate with the standard $KMnO_4$ solution[36] to the first permanent tinge of pink.

Run a determination on a sample of lead sawings free from antimony. Make correction for the blank.

Accuracy.—Duplicate titrations should not disagree more than 0.1 ml. The presence of iron and arsenic will give high figures. Copper when present to the extent of five or six per cent will impair the results.

[34] When metallic antimony is brought into solution with H_2SO_4 it dissolves according to the reaction:

(I) $$2Sb + 6H_2SO_4 = Sb_2(SO_4)_3 + 3SO_2 + 6H_2O.$$

When $Sb_2(SO_4)_3$ is titrated with $KMnO_4$ it is oxidized according to the reaction:

(II) $$5Sb_2(SO_4)_3 + 4KMnO_4 + 24H_2O = 10H_3SbO_4 + 4MnSO_4 + 9H_2SO_4 + 2K_2SO_4.$$

According to reaction (II), the valence change in antimony is two, and its chemical equivalent value is $121.76/2 = 60.88$.

The chemical equivalent value of $Na_2C_2O_4$ is $134/2 = 67$.

Hence, should 0.2 g. of $Na_2C_2O_4$ require 30 ml. of the $KMnO_4$ solution, 1 ml. of $KMnO_4 = 0.2/30 = 0.00667$ g. of $Na_2C_2O_4 = (0.00667 \times 60.88/67)$ g. of Sb.

[35] Usually a digestion of fifteen or twenty minutes suffices to completely decompose the alloy. Occasionally, the residue instead of being white is black. In that event, continue the digestion for a longer period, first adding two or three grams of Na_2SO_4. A slight discoloration will disappear when the solution is subsequently diluted and boiled, especially if the boiling is prolonged for more than five minutes. Should the residue persist in being dark-colored after prolonged boiling, the results will be erroneous.

The black coloration usually is found in those determinations where there is appreciable antimony present and large quantities of lead. A determination of an alloy containing one per cent of antimony and 99 per cent lead run on a 2 g. portion will invariably show this characteristic and give low results. The corrective measure would be to work on a 1 g. portion of such an alloy.

[36] If the HCl concentration is too high or the solution is not cold, decomposition of the $KMnO_4$ by the HCl will take place.

ARSENIC[1]

As_4, *at.wt.* 74.91—$\dfrac{\textit{cryst.}}{\textit{amorp.}}$ *sp.gr.* $\dfrac{5.73}{4.72}$ *m.p.* $\dfrac{850}{\ldots}$ *b.p.* $\dfrac{\textit{subl.}\ 554^\circ}{< 360^\circ}$; *oxides*, As_2O_3, As_2O_5.

Ores of arsenic, especially the sulfide, were known by the early Greeks and Romans and the element itself was isolated during the period of the alchemists. Arsenic is found native in limited quantities. It occurs combined with the heavy metals in form of arsenides and sulfarsenides; the trisulfide and the pentasulfide and the oxide As_2O_3, commonly known as white arsenic, are familiar compounds. Commercial minerals are realgar, As_2S_2 (red), and orpiment, As_2S_3 (yellow), smaltite, $CoAs_2$, arsenopyrite, or mispickel, FeAsS, the most common. A large number of other minerals are known.

DETECTION

Hydrogen sulfide precipitates the yellow sulfide of arsenic, As_2S_3, when passed into a solution made strongly acid with hydrochloric acid. If the solution contains more than 25% hydrochloric acid (sp.gr. 1.126), the other members of the hydrogen sulfide group do not interfere, as they are not precipitated from strong acid solutions by hydrogen sulfide. Arsenic sulfide is soluble in alkali carbonates. (Antimony sulfide, Sb_2S_3, reddish yellow, is insoluble in alkali carbonates.)

Volatility of the chloride, $AsCl_3$, is a means of separation and distinction of arsenic. Details of the procedure are given under "Separations." The distillate may be tested for arsenic as directed above.

Traces of arsenic may be detected by either the Gutzeit or Marsh test for arsenic. Directions for these tests are given at the close of the volumetric procedures.

Distinction between Arsenates and Arsenites.—Magnesia mixture precipitates white, $MgNH_4AsO_4$, when added to ammoniacal solutions containing arsenates, but it produces no precipitate with arsenites.

[1] Sulfide ores of arsenic were known by the ancient Greeks and Romans. The compounds of arsenic were recognized as poisons in mediaeval days. The element was first obtained by Albertus Magnus in the thirteenth century. The metal is used in alloys for hardening purposes, for example in lead for making of shot. Its compounds are valuable as insecticides and for pharmaceutical purposes. White arsenic is the oxide As_2O_3. In the pages following typical analyses are given for the different classes of materials in which the element is determined.

Red silver arsenate and yellow silver arsenite are precipitated from neutral solutions by ammoniacal silver nitrate. An arsenate gives a yellow precipitate with ammonium molybdate solution.

ESTIMATION

The determination of arsenic is required in the valuation of native arsenic, white arsenic, As_2O_3; ores of arsenic—orpiment, As_2S_3; realgar, As_2S_2; arsenopyrite, or mispickel, FeAsS; cobaltite or cobalt glance, CoAsS; smaltite, $CoAs_2$; niccolite, NiAs. The substance is estimated in copper ores, in speiss, regulus; in iron precipitates (basic arsenate). It is determined in paint pigments, Scheele's green, etc. The element is determined in shot alloy and in many metals. It is estimated in germicides, disinfectants, and insecticides—Paris green, lead arsenate, zinc arsenite. Traces are looked for in food products and in substances where its presence is not desired.

In the preparation of the material for analysis the volatility of arsenious chloride, $AsCl_3$, necessitates care in getting the material into solution. Arsenious solutions should not be boiled, as loss of arsenic is apt to occur, unless provision is made to prevent this. Oxidized to the quinquivalent form there is less danger of loss. Treatment with fuming nitric acid, aqua regia, fusion with a mixture of sodium carbonate and nitrate, with later conversion to chloride by action of HCl in presence of an oxidizing agent, are recommended procedures.

PREPARATION AND SOLUTION OF THE SAMPLE

In dissolving arsenic compounds it will be recalled that the oxide, As_2O_3, is not readily acted upon by dilute acids—hydrochloric or sulfuric. The compound is soluble, however, in alkali hydroxides and carbonates. Nitric acid oxidizes As_2O_3 to the higher oxide, As_2O_5, which is soluble in water. The sulfides As_2S_3 and As_2S_5 are practically insoluble in hydrochloric or sulfuric acids, but are dissolved by the fixed alkalies and alkali sulfides. All arsenites, with the exception of the alkali arsenites, require acids to effect solution.

Pyrites Ore and Arseno-pyrites.—The amount of the sample may vary from 1 to 20 grams,[1a] according to the arsenic content. The finely ground sample in a large casserole is oxidized by adding 10 to 50 ml. of bromine solution (75 ml. KBr + 50 ml. liquid Br + 450 ml. H_2O), covering and allowing to stand for

[1a] 0.1% arsenic determined on a 20-gram sample.

fifteen minutes, then 20 to 50 ml. of concentrated nitric acid are added in three or four portions, allowing the action to subside upon each addition. The glass cover is raised by means of riders, and the sample evaporated to dryness on the steam bath; 10 to 25 ml. of hydrochloric acid are now added and the sample again taken to dryness. Again 10 to 25 ml. of hydrochloric acid are added and the sample taken to dryness. Finally 25 ml. of hydrochloric acid and 75 ml. of water are added, and the mixture digested over a low flame until all the gangue, except the silica, is dissolved. The solution is now examined for arsenic by distillation of the arsenic after reduction, the distillate being titrated with standard iodine solution according to directions given later.

Arsenious Oxide.—The sample may be dissolved in caustic soda, the solution neutralized with hydrochloric acid, and the resulting sample titrated with iodine.

Fusion Method.—One gram of the finely powdered mineral is fused in a nickel crucible with about 10 grams of a mixture of potassium carbonate and nitrate, 1 : 1, and the melt extracted with hot water. Two hundred ml. of a saturated solution of SO_2 is added to the filtrate to reduce the arsenic, the excess of SO_2 then expelled by boiling, the solution diluted with dilute sulfuric acid, and arsenic determined in the filtrate.

Arsenic in Sulfuric Acid.—*Arsenious acid* may be titrated directly with iodine in a 20- to 50-gram sample, which has been diluted to 200 to 300 ml. with water and nearly neutralized with ammonium hydroxide and then an excess of sodium acid carbonate added, followed by the iodine titration.[2]

Arsenic Acid in Sulfuric Acid.—Twenty-five ml. of the acid containing about 0.1% arsenic or a larger volume in case the percentage of arsenic is less than 0.1% As_2O_3 (the sp.gr. of the acid being known) are measured out into a short-necked Kjeldahl flask. About half a gram of tartaric acid and 2 grams of fused, arsenic-free potassium bisulfate are added and the acid heated over a low flame until the liberated carbon is completely oxidized and the acid again becomes clear, e.g., a pale straw color. It is not advisable to heat to violent fuming, as a loss of arsenic is then apt to occur. The cooled acid is poured into about 300 ml. of water, the excess acid nearly neutralized with ammonia, bicarbonate of soda added in excess and the arsenious acid titrated with standard iodine. Total arsenic as As_2O_3 minus arsenious arsenic as As_2O_3 = arsenic arsenic in terms of As_2O_3. This result multiplied by 1.1618 = As_2O_5.

Arsenic in Hydrochloric Acid.—The arsenic in 20 to 100 ml. sample is reduced by ferrous chloride, the arsenic distilled according to directions given later, and the distillate titrated with iodine.

Arsenic in Organic Matter.[3]—0.2 to 0.5 gram of the sample finely powdered is oxidized by mixing with 10 to 15 grams of sodium carbonate and sodium peroxide, 1 : 1, in a nickel crucible, a portion of the fusion mixture being spread over the charge. After heating gently for fifteen minutes, the fusion is completed by heating to dull redness for five minutes longer. The contents of the crucible are rinsed into an Erlenmeyer flask after extraction with water, and the solution made acid with dilute sulfuric acid, 1 : 1. The mixture is boiled down to 100 ml., 1 to 2 grams of potassium iodide added and the solu-

[2] SO_2 should be expelled by heat or by a current of air before treating with the alkali.

[3] Organic matter may be destroyed by heating the substance on addition of 10% H_2SO_4 and solid $(NH_4)_2S_2O_8$.

tion further concentrated to about 40 ml. Iodine is reduced with sulfurous acid or thiosulfate, the solution diluted with hot water and saturated with hydrogen sulfide. Arsenious sulfide is filtered off, washed, dissolved in 15 to 20 ml. of half-normal sodium hydroxide and 30 ml. of hydrogen peroxide (30%) solution added, and the solution boiled. About 12 ml. of dilute sulfuric acid, 1 : 1, are added, together with 1 to 2 grams of potassium iodide, the solution concentrated to 40 ml. and free iodine reduced with thiosulfate as before. Arsenic is now titrated, with standard iodine, upon neutralization of the free acid with sodium hydroxide and sodium acid carbonate.

Lead Arsenate.—Ten grams of the thoroughly mixed paste or 5 grams of the powder are dissolved by treating with 25 ml. of 10% hot sodium hydroxide solution, and diluted to 250 ml. An aliquot part, 50 ml. (=2 grams paste and 1 gram powder), is placed in an Erlenmeyer flask and 20 ml. of dilute sulfuric acid, 1 : 1, added, and the solution diluted to 150 ml. About 3 grams of solid potassium iodide are added and the solution boiled down to about 50 ml. (but not to fumes). The liquor will be colored yellow by free iodine. Tenth normal sodium thiosulfate is added drop by drop until the free iodine is neutralized (solution loses its yellow color), it is now diluted to about 250 ml. and the free acid neutralized by ammonium hydroxide (methyl orange indicator), then made slightly acid with dilute sulfuric acid, and an excess of bicarbonate of soda added. The arsenic is titrated with standard iodine.

The arsenic may be reduced by placing the 50-ml. sample in a Kjeldahl flask, adding 25 ml. of concentrated sulfuric acid (1.84 sp.gr.), $\frac{1}{2}$ gram tartaric acid and 2 grams acid potassium sulfate, $KHSO_4$, and digesting over a strong flame until the organic matter is destroyed and the solution is a pale yellow color. The cooled acid is diluted and neutralized, etc., as directed above.

Water-soluble Arsenic in Insecticides. Rapid Works Test.—Two grams of the paste is digested with 1000 ml. of water at 90° C. for five minutes, in a graduated 1000-ml. flask. An aliquot portion is filtered and the arsenic determined by the Gutzeit method.

Water-soluble arsenite may be titrated directly with iodine in presence of sodium bicarbonate.

Zinc Arsenite.—About 5 grams of powder or 10 grams of paste are taken and dissolved in a warm solution containing 300 ml. of water and 25 ml. of strong hydrochloric acid. The cooled solution is diluted to 500 ml. and 100 ml. portions taken for analysis. The acid is partly neutralized with ammonium hydroxide and 50 ml. of a saturated solution of ammonium oxalate added (to prevent precipitation of the zinc as $ZnCO_3$), and an excess of sodium bicarbonate, $NaHCO_3$. Arsenic is now titrated with iodine as directed later.

Soluble Arsenic in Zinc Arsenite.—One gram sample is rubbed into an emulsion with several portions of water until the whole is in suspension. The cloudy liquor is diluted to 1000 ml. and a portion filtered through a $\frac{1}{4}$-in. asbestos mat on a perforated plate, the asbestos being covered with a layer of filter paper. The first 50 ml. are rejected. One hundred ml. of the clear filtrate (=0.1 gram) is treated with 10 ml. of strong sulphuric acid, 0.05 gram, Fe_2O_3 (use ferric ammonium sulfate) and $\frac{1}{2}$ ml. of 80% stannous chloride solution and heated until colorless. Arsenic is now determined by the Gutzeit method, using the larger-sized apparatus.

Arsenic Acid, Alkali Arsenates, etc.—The sample is dissolved in 20 to 25 ml. of dilute sulfuric acid, 1 : 1, in an Erlenmeyer flask, and reduced by addition of 3 to 5 grams of potassium iodide, the action being hastened by placing the mixture on a steam bath. The iodine liberated is exactly neutralized with thiosulfate and the arsenious acid titrated with iodine according to the procedure given later.

Arsenic in Steel, Iron, Pig Iron, etc.—One to 50 grams of steel, etc., may be treated according to the scheme for pyrites. If a large sample is taken, it is advisable to treat it in a 500-ml. flask, connected with a second flask containing bromine, to guard against loss of arsenic by volatilization. When the sample has dissolved it is taken to dryness (the bromine in the second flask being combined with it) and treated as directed in pyrites. Arsenic chloride, $AsCl_5$, is transferred to the distilling flask with strong hydrochloric acid, and arsenic separated from the iron by volatilization of reduced chloride according to the procedure given below.

Arsenic in Copper.—Arsenic is precipitated with iron by the basic acetate method, and thus freed from copper. Details of procedure are given under the determination of impurities in copper in the chapter on the subject.

NOTES.—In the decomposition of the sample Low recommends the addition of a little sodium sulfide to ores containing oxides. To prevent loss of arsenic during the treatment with H_2S he uses a flask with a two-hole rubber stopper through which passes an inlet tube reaching to the bottom of the flask and an exit tube, the latter a thistle tube containing a little absorbent cotton soaked with dilute NaOH to retain any arsenic escaping from the flask.

Iron sulfate dissolves slowly, so that if much is present in the ore time must be allowed for this to dissolve.

As arsenious chloride is volatile, great care must be exercised in heating solutions containing HCl and arsenious salts as a loss will occur. B.p. 130.2° C.

The ore may be brought into solution by fusion with a mixture of sodium carbonate, potassium nitrate and zinc oxide, 1 : 1 : 2, the fusion being made in a platinum dish. The potassium iodide procedure may be followed for reduction of arsenic. (See Lead Arsenate.)

Organic Substances.—The fuming sulfuric acid—30% hydrogen peroxide method of decomposition which has been described on page 67 for antimony compounds may also be used for organic compounds containing arsenic.

SEPARATIONS

Isolation of Arsenic by Distillation as Arsenious Chloride [4]

By this method arsenic may be separated from antimony, tin, and from other heavy metals. It is of special value in the direct determination of arsenic in iron ores, copper ores, and like products and has a wide application. The procedure depends upon the volatility of arsenious chloride at temperatures lower than the other heavy metals. In a current of HCl gas, arsenious chloride begins to volatilize below 108° C., and is actively volatile at 120° C.; antimony starts to volatilize at 110° C., but is not actively volatile until a temperature of 180° C. has been reached. The boiling-point of arsenious chloride, $AsCl_3$, is 130.2° C.; antimony trichloride, $SbCl_3$, is 223.5° C.; and that of stannous

[4] J. E. Stead's Method. R. C. Roark and C. C. McDonnell, J. Ind. Eng. Chem., 8, 327, 1916.

chloride, $SnCl_2$, is over 603° C.; other chlorides having still higher boiling-points. Tin in its higher form, $SnCl_4$, is readily volatile, boiling-point is 114° C., so that it is necessary to have it in its bivalent form to effect a separation from arsenic. When heavy metals are present in the residue remaining from the arsenic distillate, or when zinc chloride is added to raise the boiling-point, antimony may also be separated by distillation by carrying the solution to near dryness, adding concentrated HCl by means of a separatory funnel, drop by drop, during further distillation of the concentrate. Arsenic may be determined in the distillate (first portions) either gravimetrically or volumetrically.

Procedure.—If arsenic is present as arsenic chloride, as prepared in the method for solution of iron ores, the sample may be transferred directly to the distillation flask by means of concentrated, arsenic-free hydrochloric acid.

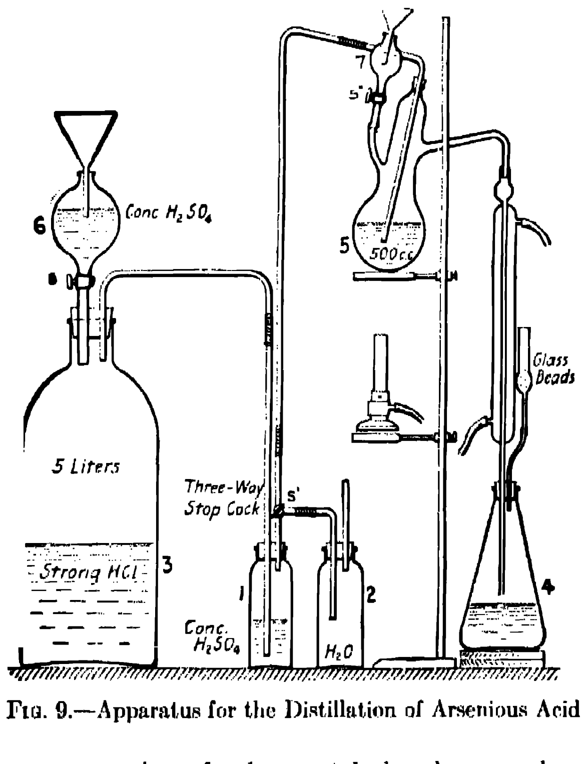


FIG. 9.—Apparatus for the Distillation of Arsenious Acid.

If a preliminary separation of other metals has been made and arsenic is present (along with antimony and tin) as a sulfide, it is oxidized by addition of concentrated HCl and sufficient potassium chlorate to cause solution and oxidation of free sulfur, and the chlorate decomposed by evaporation to dryness; or if preferred, by evaporation of the alkaline solution to dryness, oxidation with fuming nitric acid and re-evaporation to dryness to expel the nitric acid. The residue is taken up with hydrochloric acid and washed into the flask with strong hydrochloric acid as directed above.

Distillation.—The sample, in a half-liter distilling flask (Fig. 9), is made up to about 150 ml. with concentrated hydrochloric acid and about 15–20

grams of cuprous chloride are added. In place of Cu_2Cl_2 hydrazine sulfate may be used—add first 0.5 g. of NaBr, followed by 0.5 g. $(NH_2)_2SO_4$. The apparatus is connected up as shown in the illustration, Fig. 9. The end of the condenser dips into 400 ml. of cold water in a large beaker or flask. The solution is cooled by placing it in ice-water or cold running water. The sample is saturated with dry hydrogen chloride gas generated by dropping concentrated sulfuric acid into concentrated hydrochloric acid saturated with ammonium chloride. When the point of saturation is reached the gas begins to bubble through the solution instead of being absorbed by it. When this occurs, heat is applied and the solution brought to boiling, the current of HCl gas being continued. At a temperature below 108° C. to 110° C. the first 100 ml. will contain practically all of the arsenic. About two-thirds of the solution is distilled off. It is advisable to add more hydrochloric acid to the residue in the flask, together with cuprous chloride, and repeat the distillation into a fresh lot of water. This may be done during the estimation of arsenic in the first distillate.

Arsenic may be determined in the distillates either gravimetrically or volumetrically. The volumetric procedures for arsenic, in this isolated form, are generally to be preferred, since they are both rapid and accurate. For amounts over 0.5% arsenic, the iodine method is recommended, for smaller amounts (arsenic in crude copper), precipitation with silver nitrate and titration of the silver salt is best. Exceedingly small amounts are best determined by the Gutzeit method.

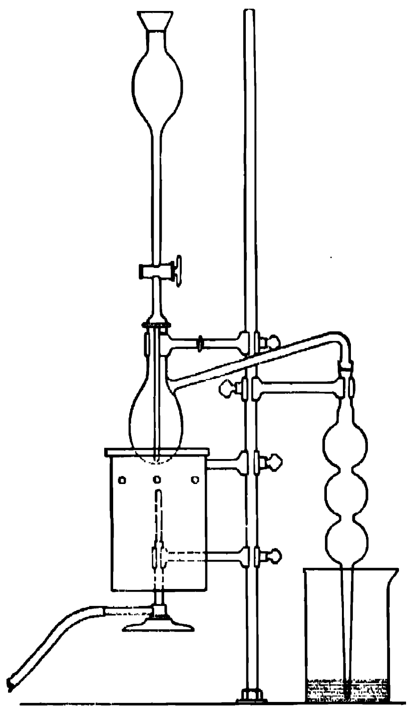


Fig. 10.—Knorr Arsenic Distillation Apparatus.

In place of the large bottle, a smaller wash bottle may be used filled with concentrated hydrochloric acid. The bottle contains an inlet tube dipping to the bottom and an exit tube connected to the distillation flask containing the arsenic. The receiving flask is connected with an aspirator and air drawn through the system. HCl is swept into the distillation flask during the arsenic distillation, keeping the solution concentrated with HCl gas.

The inlet funnel is filled about half full with hydrochloric acid (sp.gr. 1.2). The outlet of the condenser tube is caused to dip just beneath the surface of 100 ml. of distilled water, containing a lump of ice. The solution in the distillation flask is heated to boiling; concentrated hydrochloric acid is introduced through the funnel drop by drop at a rate sufficient to replace the evaporation. All the arsenic usually distills over in half an hour. At this time the beaker holding the condensate is replaced by another with 100 ml.

of water and the distillation continued about 15 minutes. Test this distillate to ascertain whether any arsenic is present. The arsenious chloride thus obtained is titrated. The free HCl is first neutralized with a fixed alkali and then made faintly acid with HCl. Sodium bicarbonate is now added in excess and the titration with iodine made according to the customary procedure. If desired the arsenic may be determined as sulfide by precipitating as As_2S_3 with H_2S in a 9N HCl solution.

Commercial hydrochloric acid invariably contains arsenic, so this must be purified by redistillation in presence of an oxidizing agent to oxidize the arsenic to the non-volatile arsenic pentachloride, $AsCl_5$, form (Fig. 13), or by treatment with H_2S and filtration. A blank run should be made on the reagents used, especially when traces of arsenic are to be determined.

Cuprous Chloride.—This is used to reduce arsenic. At least 2 grams CuCl should be used per each gram of iron present. In the distillation, HCl gas (generated in a flask containing concentrated sulfuric acid by allowing hydrochloric acid to flow in through a thistle tube, drop by drop) may be passed into the solution containing the arsenic, in place of adding concentrated hydrochloric acid.

Hydrazine Distillation Method.—Weigh a suitable amount of sample into a 275 ml. Pyrex sulfur flask. Treat with a small amount of HNO_3 (5–10 ml.), and a pinch of potassium chlorate. Take to dryness. Add 3–5 ml. HCl and take again to dryness. Add 20 ml. 1 : 1 HCl and boil several minutes. Filter, if insoluble is appreciable, into another flask, and wash. Add 30 ml. HCl, ½ g. NaBr and ½ g. hydrazine sulfate, $(NH_2)_2SO_4$. Set the flask on a small electric plate, and at the same time, insert in the flask a two-hole stopper, in one hole of which is a separatory funnel, and in the other a glass tube leading to an 8-in. Allihn condenser, set vertically. The lower end of the condenser is immersed in cold water contained in a No. 3 beaker, which sits on a block of wood. Have the cock of the funnel open. Have a good stream of cold water running through the jacket of the condenser.

Distill until the volume in the flask has been reduced to 20 ml. Close the cock of the funnel, add 20 ml. HCl, remove the block of wood from underneath the beaker and hold the beaker in one hand. Holding the beaker at such a height that no liquid may be sucked back into the flask, open the funnel cock and let the acid run into the flask. Now, place the block under the beaker, and distill until liquid in flask is again reduced to 20 ml.

Remove the flask from the plate, and disconnect it from the condenser. Wash the condenser, allowing washings to run into the distillate. Remove the beaker from under the condenser. Add 8–10 drops of methyl orange (1 g. of salt per liter of water). Make the solution alkaline with NH_4OH, then just acid with HCl. Cool. Add 10 g. $NaHCO_3$ and 10 ml. starch solution (10 g. soluble starch boiled in a liter of water; cooled).

Titrate with iodine solution, one ml. of which equals about .005 g. As_2O_3. Subtract a blank determination which amounts to .4 or .5 ml.

A procedure for the successive distillation of arsenic, antimony, and tin has been described in the Chapter on Antimony, p. 69.

Separation of Arsenic from Antimony and Tin by Precipitation as Sulfide in a Concentrated Hydrochloric Acid Solution

This procedure for isolation of arsenic depends upon the insolubility of the sulfide of arsenic in concentrated hydrochloric acid, whereas that of antimony dissolves. The sulfide of tin is also soluble.

Procedure.—The metals present in their lower conditions of oxidation are precipitated as sulfides in presence of dilute hydrochloric acid (5% solution) to free them from subsequent groups (Fe, Al, Ca, etc.). The soluble members of the hydrogen sulfide group are now dissolved and separated from copper, lead, etc., by caustic as follows: The greater part of the washed precipitate is transferred to a small casserole, that remaining on the filter paper is dissolved off by adding to it a little hot dilute potash solution, catching the filtrate in the casserole. About 5 grams weight of solid potassium hydroxide or sodium hydroxide is added to the precipitate. Arsenic, antimony, and tin sulfides dissolve. The solution is filtered if a residue remains, and the filter washed. This preliminary treatment is omitted if alkaline earths and alkalies are the only contaminating elements present.

The casserole containing the sample is covered and placed on a steam bath. Chlorine is now conducted into the warm solution for an hour, whereby the alkali is decomposed and antimony and arsenic oxidized to their higher state. Sufficient hydrochloric acid is added to decompose the chlorate formed, and the uncovered solution evaporated to half its volume. An equal volume of hydrochloric acid is added and the evaporation repeated, to expel the last trace of chlorine. The acid solution is washed into an Erlenmeyer flask, cooled by ice to 0° C. and two volumes of cooled, concentrated, hydrochloric acid added. H_2S gas is rapidly passed into this solution for an hour and a half. The flask is now stoppered and placed in boiling water for an hour. The yellow arsenic sulfide, As_2S_5, is filtered through a weighed Gooch crucible, washed with hydrochloric acid, 2 : 1, until free from antimony, i.e., the washing upon dilution remains clear. The residue is now washed with water, followed by alcohol, and may be dried and weighed as As_2S_5, or determined volumetrically. Antimony and tin are determined in the filtrate. McCay recommends washing As_2S_5 with alcohol, CS_2 and finally alcohol.[5]

The sulfide may be dissolved in concentrated sulfuric acid by heating to sulfuric acid fumes and until the solution becomes clear. No arsenic is lost, provided the heating is not unduly prolonged. Fifteen to twenty-five minutes is generally sufficient to dissolve the sulfide and expel SO_2, etc. The acid may be neutralized with ammonia or caustic, made again barely acid and then alkaline with bicarbonate of soda, and arsenious acid titrated with iodine.[6]

The separation of arsenic from tin by precipitation as arsenious sulfide in dilute hydrofluoric acid solution has been described under antimony, page 71.

[5] Le Roy W. McCay, Chem. News, 56, 262, 1887.
[6] J. and H. S. Pattinson, Jour. Soc. Chem. Ind., 1898, p. 211.

GRAVIMETRIC METHODS FOR DETERMINATION OF ARSENIC

As in the case of antimony, the accuracy and rapidity of the volumetric methods for the determination of arsenic make these generally preferable to the more tedious gravimetric methods. The following methods, however, are of value in certain analytical procedures.

DETERMINATION OF ARSENIC AS THE TRISULFIDE, As_2S_3

Arsenic acid and arsenates should be reduced to the arsenious form before precipitation as the sulfide. The procedure is especially adapted to the isolation of arsenic from other elements, when this substance is present in the solution in appreciable quantities, advantage being taken of the extreme difficulty with which arsenious sulfide, As_2S_3, dissolves in hydrochloric acid solution.

Procedure.—The solution containing arsenic in the arsenious form, strongly acid with hydrochloric acid (9N HCl), is saturated with H_2S at room temperature. The hydrogen sulfide pressure generator is recommended for this treatment (Figs. 11 and 12). The precipitate is filtered into a weighed Gooch crucible (previously dried at 105° C.). The As_2S_3 is washed with HCl that has been saturated with H_2S, then with alcohol, followed by CS_2 to remove free S and finally again with alcohol. The compound dried at 105° C. to constant weight is weighed as As_2S_3.

Factors. $As_2S_3 \times 0.6090 =$ grams As.
$As_2S_3 \times 0.8041 =$ grams As_2O_3.
$As_2O_3 \times 1.1618 =$ grams As_2O_5.
$As_2O_5 \times 1.3135 =$ grams $H_3AsO_4 . \frac{1}{2}H_2O$.
$As_2S_3 \times 1.2606 =$ grams As_2S_5.

If a preliminary separation of $AsCl_3$ by distillation was made the arsenic will be in form for this method.

NOTE.—Arsenic may also be determined as arsenic sulfide by passing a rapid stream of H_2S into a cooled solution of arsenic acid containing at least two parts of concentrated hydrochloric acid for each part of water present in the solution.

DETERMINATION OF ARSENIC AS MAGNESIUM PYROARSENATE

The method worked out by Levol depends upon the precipitation of arsenic as $MgNH_4AsO_4 \cdot 6H_2O$, when magnesia mixture is added to an ammoniacal solution of the arsenate. Although 600 parts of water dissolve 1 part of the salt, it is practically insoluble in a $2\frac{1}{2}$ per cent ammonia solution, 1 part of the anhydrous salt requiring 24,558 parts of the ammonia water according to Virgili.[7] The compound loses $5\frac{1}{2}$ molecules of water at 102° C. and all of the water when strongly ignited, forming in presence of oxygen the stable magnesium pyroarsenate, $Mg_2As_2O_7$, in which form arsenic is determined.

[7] Average of three results. J. F. Virgili, Z. anal. Chem., **44**, 504, 1905.

Figure 11 shows a convenient form of a generator for obtaining hydrogen sulfide gas under pressure. The apparatus is the writer's modification of the Banks' generator sold by E. and A. and is designed for large quantities of hydrogen sulfide gas. The cylinder *A A'* is constricted, as shown, to support perforated lead disk *G*, upon which rests the iron sulfide. The lower end of the chamber is closed to catch small particles of FeS that may be carried through the perforations of the disk. Small openings admit the acid to *A'*. The level of the acid is below the disk *G*, so that the acid only comes in contact with the sulfide when pressure is applied by means of the rubber bulb *E*, the stopcock S^1 being open and S^3 closed. The mercury gauge *C* is adjusted to blow out at a given pressure, to prevent accident, the bulb *D* preventing the mercury from being blown out of the apparatus. A small opening in *D* allows the escape of the gas. When

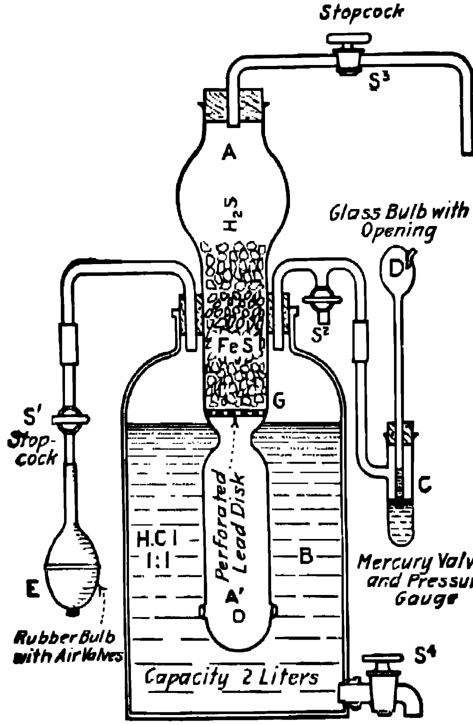


Fig. 11.—Scott's Hydrogen Sulfide Generator.

the apparatus is in operation, *H* is connected to an empty heavy-walled bottle, which in turn is attached with glass tube connection to the pressure flask in which the precipitation of the sulfide is made, the flask being closed to the outside air. By pressure on the rubber bulb *E*, acid is forced into the chamber *A'* past the disk into the sulfide in *A*. The entire system will now be under the pressure indicated by the gauge *C*. The pressure is released by opening the stopcock S^2 and the flask containing the precipitate then disconnected. The reservoir is designed to hold about two liters of acid, and the cylinder containing the sulfide is of sufficient capacity to hold over one pound of FeS, so that the apparatus will deliver a large quantity of hydrogen sulfide.

Procedure.—The solution containing the arsenic, in the form of arsenate, and having a volume not exceeding 100 ml. per 0.1 gram arsenic present, is treated with 5 ml. of concentrated hydrochloric acid, added, with constant stirring, drop by drop. Ten ml. of magnesia mixture are added (Reagent=55 grams $MgCl_2$+70 grams NH_4Cl+650 ml. H_2O and made up to 1000 ml. with NH_4OH, sp.gr. 0.96), for each 0.1 gram of arsenic present. Ammonia solution

(sp.gr. 0.96) is added from a burette, with stirring, until the mixture is neutralized (a red color imparted to the solution in presence of phenolphthalein indicator), and then ammonia added in excess equal to one-third the volume of the neutralized solution. The precipitate is allowed to settle at least twelve hours and is then filtered into a weighed Gooch crucible and washed with 2.5% ammonia until free from chloride. After draining as completely as possible by suction the precipitate is dried at 100° C. and then heated to a dull red heat (400 to 500° C.), preferably in an electric oven, until free of ammonia. The temperature is then raised to a bright red heat (800 to 900° C.) for about ten minutes, the crucible then cooled in a desiccator and the residue weighed as $Mg_2As_2O_7$.

Factors, $Mg_2As_2O_7 \times 0.4826 = As$, or $\times 0.6372 = As_2O_3$, or $\times 0.7403 = As_2O_5$, or $\times 0.7924 = As_2S_3$.

Notes.—In place of an electric furnace the Gooch crucible may be placed in a larger non-perforated crucible, the bottom of the Gooch being 2–3 mm. above the bottom of the outer crucible. The product may now be heated in presence of a current of oxygen passed through a perforation in the covering lid of the Gooch, or in place of the oxygen, a thin layer of powdered NH_4NO_3 may be placed on the arsenate residue and the heat gradually applied until the outer crucible attains a light red glow.

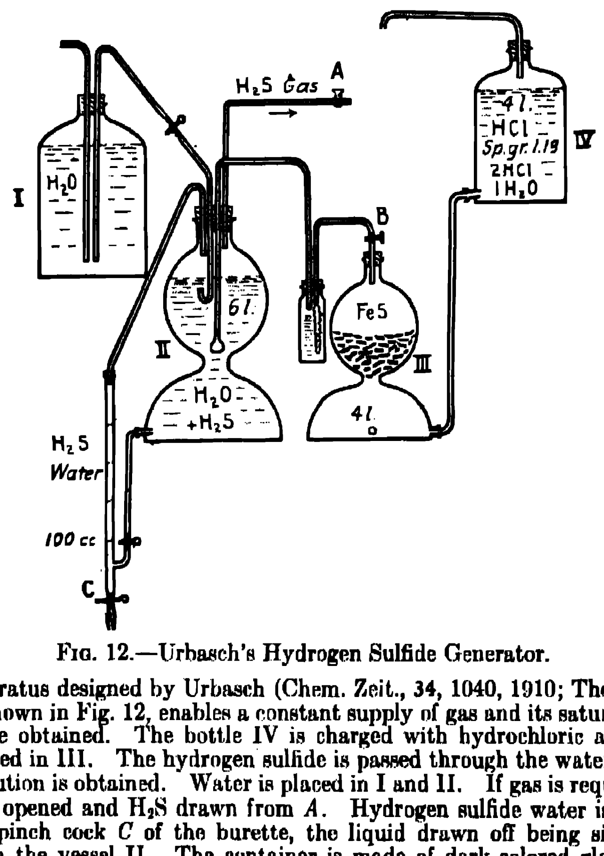


Fig. 12.—Urbasch's Hydrogen Sulfide Generator.

The apparatus designed by Urbasch (Chem. Zeit., 34, 1040, 1910; The Analyst, 35, 558, 1910), shown in Fig. 12, enables a constant supply of gas and its saturated aqueous solution to be obtained. The bottle IV is charged with hydrochloric acid, and iron sulfide is placed in III. The hydrogen sulfide is passed through the water in II until a saturated solution is obtained. Water is placed in I and II. If gas is required the taps *A* and *B* are opened and H_2S drawn from *A*. Hydrogen sulfide water is obtained by opening the pinch cock *C* of the burette, the liquid drawn off being simultaneously replaced from the vessel II. The container is made of dark-colored glass to protect the hydrogen sulfide water from light. Water may be drawn into II, when required by opening the pinch cock leading to the bottle I.

VOLUMETRIC METHODS FOR THE DETERMINATION OF ARSENIC

OXIDATION OF THE ARSENIOUS ACID WITH STANDARD IODINE [8]

This procedure is applicable for the determination of arsenic in acids, after reduction of arsenic to its arsenious form, for valuation of arsenic in the trioxide, for determination of arsenic isolated by distillation as arsenious chloride, for arsenic in arsenites and reduced arsenates in insecticides, etc. The method depends upon the reaction—$As_2O_3+2H_2O+2I_2=As_2O_5+4HI$. The liberated hydriodic acid is neutralized by sodium bicarbonate. The trace of excess iodine is detected by means of starch, a blue color being produced.

Procedure.—If the solution is acid, it is neutralized by sodium or potassium hydroxide or carbonate (phenolphthalein indicator) then made slightly acid. If the solution is alkaline, it is made slightly acid. Two to 3 grams of sodium bicarbonate are added together with starch indicator and the solution titrated with tenth normal iodine solution, the iodine being added cautiously from a burette until a permanent blue color develops.

One ml. N/10 iodine = 0.003746 gram As, or 0.004946 gram As_2O_3.
$As_2O_3 \times 1.1618 = As_2O_5$. $As \times 1.3204 = As_2O_3$ or $\times 1.534 = As_2O_5$.
$As_2O_3 \times 0.7574 = As$.

NOTE.—A blank run should be made of the reagents used and this blank subtracted from the results obtained.

IODINE METHOD IN THE PRESENCE OF MERCURIC SALTS

If mercuric chloride is present in a solution containing trivalent arsenic or antimony and hydrochloric acid in concentrations from 1–3N, it is possible to titrate with standard iodine solution using carbon tetrachloride as indicator, or using the potentiometric method of indication.[9]

Procedure.—Add to the arsenic solution, which is placed in a 250-ml. glass-stoppered bottle or flask, 50 ml. of saturated mercuric chloride solution and enough hydrochloric acid to make the concentration 1.2 to 1.7 N. Add 15 or 20 ml. of carbon tetrachloride for purposes of indication. Titrate with the iodine solution, shaking the stoppered bottle very thoroughly between additions of reagent near the end point, which is the appearance of the iodine color in the carbon tetrachloride layer.

POTASSIUM IODATE METHOD FOR DETERMINING ARSENIC [8]

The method is specially applicable to determining arsenic in insecticides. The reaction is represented as follows:

$$As_2O_3+KIO_3+2HCl=As_2O_5+ICl+KCl+H_2O.$$

[8] Geo. S. Jamison, J. Ind. Eng. Chem., **10**, 290–292, 1918.
[9] Furman and Miller, J. Am. Chem. Soc., **59**, 152 (1937).

Procedure.—In determining total arsenic the sample is placed in a distilling bulb, connected to a condenser, concentrated hydrochloric acid added together with cuprous chloride, and arsenious chloride distilled over into an Erlenmeyer flask according to the standard procedure outlined. If arsenic is high, an aliquot portion of the distillate is taken and the titration made with standard iodate solution as stated later.

For determining arsenious oxide in Paris Green or other arsenite 0.15 to 0.4 grams of the sample may be weighed directly into a glass-stoppered bottle (500 ml.) and the titration made.

Iodate Titration.—30 ml. of hydrochloric acid sp.gr. 1.19, 20 ml. of water and 6 ml. of chloroform are added to the solid arsenite. If the arsenic is in solution, sufficient HCl should be present to have the acidity between 11 and 20 per cent HCl. (If this falls below 11% HCl hydrolysis of the iodine monochloride will take place. If over 20% HCl the reaction proceeds very slowly.) Potassium iodate solution is now added, rapidly at first, shaking the contents of the bottle. When the iodine that has been liberated during the first part of the titration has largely disappeared from the solution, the stopper of the bottle is inserted and the contents thoroughly shaken. The titration is now conducted cautiously, shaking thoroughly with each addition of the reagent. The titration is complete when after shaking and allowing to stand 5 minutes no color is observed in the chloroform.

Reagent.—Contains 3.245 g. of KIO_3 (dried at 140° C.) per 1000 ml.—1 ml. = 0.003 g. As_2O_3.

Other Oxidation Methods.—Standard potassium bromate may be used to titrate trivalent arsenic in exactly the same way in which it is used to determine antimony. See Chapter on Antimony.

The selective titration of antimony in the presence of arsenic with standard ceric sulfate has been described in the Chapter on Antimony. For the titration of arsenic, the best procedure is that of Gleu.[10]

VOLUMETRIC DETERMINATION OF ARSENIC BY PRECIPITATION AS SILVER ARSENATE

Bennett's modification of Pearce's method, combining Volhard's, depends upon precipitation of arsenic, from a solution neutralized with acetic acid, by addition of neutral silver nitrate solution; the silver arsenate is dissolved in nitric acid, and the silver titrated with standard thiocyanate.

Procedure.—0.5 gram, or less, of the finely powdered substance is fused with 3 to 5 grams of a mixture of sodium carbonate and potassium nitrate (1 : 1) about one-third being used on top of the charge. The cooled mass is extracted with boiling water and filtered. The filtrate, containing the alkali arsenate, is strongly acidified with acetic acid, boiled to expel the carbon dioxide, then cooled and treated with sufficient sodium hydroxide solution to give an alkaline reaction to phenolphthalein indicator. The purple red color is now discharged from the solution by addition of acetic acid. A slight excess of neutral silver nitrate is vigorously stirred in and the precipitate allowed to settle in the dark. The supernatant liquid is poured off through a filter and the precipitate washed

[10] Gleu. Z. anal. Chem., 95, 305 (1933). See Chapter on Standard Solutions.

by decantation with cold distilled water, then thrown on the filter and washed free of silver nitrate solution. The funnel is filled with water and 20 ml. of concentrated nitric acid added. The dissolved silver arsenate is caught in the original beaker in which the precipitation was made, the residue on the filter washed thoroughly with cold water and the filtrate and washings made up to 100 ml. The silver is now titrated by addition of standard ammonium or potassium thiocyanate, until a faint red color is evident, using ferric ammonium alum indicator, according to the procedure described for determination of silver. (See Chlorine and Silver Chapters.)

One ml. N/10 thiocyanate = 0.010788 gram Ag.
Factor. $Ag \times 0.2315 = As$.

NOTE.—The silver arsenate salt is nearly six times the weight of arsenic, so that very small amounts of arsenic may be determined by the procedure, hence it is not necessary to use over 0.5 gram of the material. For traces of arsenic the Gutzeit method, following, should be used.

Small amounts of Ge, Sb, Sn do not interfere. Chromates, molybdates, phosphates, tungstates, vanadates should be absent as these precipitate as silver salts. An excessive amount of ammonium salt has a solvent action on silver arsenate.

DETERMINATION OF SMALL AMOUNTS OF ARSENIC

MODIFIED GUTZEIT METHOD

The following procedure furnishes a rapid and accurate method for determination of exceedingly small amounts of arsenic ranging from 0.001 milligram to 0.5 milligram As_2O_5. It is more sensitive and less tedious than the Marsh test. The details, given below with slight modifications, have been carefully worked out in the laboratories of the General Chemical Company [11] and have proved exceedingly valuable in estimating small amounts of arsenic in acids, bases, salts, soluble arsenic in lead arsenate and zinc arsenite and other insecticides, traces of arsenic in food products, baking powders, canned goods, etc.

The method depends upon the evolution of arsine by the action of hydrogen on arsenic compounds under the catalytic action of zinc, the reaction taking place either in alkaline or acid solutions. The evolved arsine reacts with mercuric chloride, forming a colored compound. From the length and intensity

[11] Evolution of arsine by the electrolytic method, in place of the method outlined, proved to be unreliable. The evolution of arsine is effected by the slightest variation in conditions so it is extremely difficult to obtain concordant results.

of the color stain the amount of arsenic is estimated by comparison with standard stains.

Although the acidity of the sample and the amount of zinc shot should be kept within certain limits, the results are not affected by slight variation as was formerly thought. The physical characteristics of the zinc used rather than the surface exposed to acid action appears to have an effect on the evolution of arsine. The best results are obtained with zinc having a fine crystalline structure.

Iron present in the solution tends to prevent evolution of stibine, but has no apparent effect on arsine generation.

Stannous chloride is essential to the complete evolution of arsine, hence this reagent is added to the solution in which arsenic is determined.

Antimony present in the solution in amounts less than 0.0001 gram, does not interfere with the determination of arsenic. If a greater amount of antimony is present a separation of arsenic should be made by distillation. The following modification of the method is recommended. In place of the generator for HCl shown in Fig. 9, air saturated with HCl, by passing it through a gas wash bottle containing concentrated hydrochloric acid, is drawn through the boiling solution containing the sample in a saturated HCl solution, reduction of arsenic to arsenious chloride having been effected with cuprous chloride as prescribed. The air sweeps the arsine into the water in the receiving flasks (Fig. 9). It is advisable to have two flasks connected in series in place of one as shown. Gentle suction is applied at the receiving end of the train. The apparatus may be made in fairly compact form.

NOTES.—An accuracy of ±0.002 mg. to ±0.004 mg. can be obtained by this method.

Interferences.—HNO_3, Cl, Br, I, H_2S, SO_2, PH_3 must be absent. Hg, Pt, Ag, Pd, Ni, Co, $CuSO_4$ are undesirable. Sb should not exceed 0.1 mg.

Special Reagents. ***Standard Arsenic Solution.***—One gram of resublimed arsenious acid, As_2O_3, is dissolved in 25 ml. of 20% sodium hydroxide solution (arsenic-free) and neutralized with dilute sulfuric acid. This is diluted with fresh distilled water, to which 10 ml. of 95% H_2SO_4 has been added, to a volume of 1000 ml. Ten ml. of this solution is again diluted to a liter with distilled water containing acid. Finally 100 ml. of the latter solution is diluted to a liter with distilled water containing acid. One ml. of the final solution contains 0.001 milligram As_2O_3.

Standard Stains.—Two sets of stains are made, one for the small apparatus for determining amounts of As_2O_3 ranging from 0.001 to 0.02 milligram, and a second set for the larger-sized apparatus for determining 0.02 to 0.5 milligram As_2O_3. Stains made by As_2O_3 in the following amounts are convenient for the standard sets; e.g., small apparatus, 0.001, 0.002, 0.004, 0.006, 0.01, 0.15, 0.02 milligram As_2O_3. Large apparatus, 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 milligram As_2O_3.

In making the stain the requisite amount of standard reagent, As_2O_3 solution, is placed in the Gutzeit bottle with the amounts of reagents prescribed for the regular tests and the run made exactly as prescribed in the regular procedure.

Preservation of the Stains.—The strips of sensitized paper with the arsenic stain are dipped in molten paraffine (free from water), and mounted on a sheet of white paper, folded back to form a cylinder. The tube is placed in a glass test-tube containing phosphorus pentoxide, which is then closed by a stopper. It is important to keep the stained strips dry, otherwise the stain soon fades, hence the paper on which the strips are mounted and the glass test-tube, etc., must be perfectly dry. It is advisable to keep the standard in a hydrometer case, while not in use, as light will gradually fade the color.

Sensitized Mercuric Chloride (or Bromide) Paper.—20×20 in. Swedish Filter Paper No. 0 is cut into four equal squares. For use in the large Gutzeit apparatus the paper is dipped into a 3.25% solution of mercuric chloride (mercuric bromide may be used in place of the chloride) or if it is to be used in the small Gutzeit apparatus it is dipped into a 0.35% mercuric chloride solution. (The weaker the solution, the longer and less intense will be the stain.) The paper should be of uniform thickness, otherwise there will be an irregularity in length of stain for the same amounts of arsenic. (The thicker the paper the shorter the stain.) The paper is hung up and dried in the air, free from gas fumes, H_2S being particularly undesirable. When dry, half an inch of the outer edge is trimmed off (since this is apt to contain more of the reagent), and the paper cut into strips. The paper with more concentrated reagent is cut into strips 15 cm. by 5 mm. and that with 0.35% mercuric chloride into strips 12 cm. by 2.5 mm. The paper is preserved in bottles with tight-fitting stoppers. Standards should be made with each batch of paper. Paper with a white deposit of $HgCl_2$ should not be used.[12]

Mercuric Bromide Paper.—Kemmerer and Schrenk (G. Kemmerer, H. H. Schrenk, Ind. Eng. Chem., **18**, 707, July, 1926) recommend that the paper that is to be sensitized be dried at 105° C. for 1 hour and stored in a desiccator over $CaCl_2$. The paper is cut into 2.5 mm. strips and saturated with a 1.5% solution of mercuric bromide in 95% ethyl alcohol. After draining the strips are dried in a desiccator for 10 minutes and used. The treated strips should not be stored for longer than 2 hrs. before use.

In the *Marsh* test arsine is passed through a glass tube constricted to capillarity. By application of heat the arsine is decomposed and metallic arsenic deposited. The tube is heated just before the capillary constriction so that arsenic deposits in the drawn out tube. Comparison is made with standards, the length of the stain being governed by the amount of arsenic in the evolved gas. Slight variations in the size of the capillary tube and rate of evolution make a notable variation in length of stain.

Ferric Ammonium Alum.—Eighty-four grams of the alum with 10 ml. of mixed acid is dissolved and made up to a liter. Ten ml. of this solution contains approximately 0.5 gram Fe_2O_3.

Lead Acetate.—One per cent solution with sufficient acetic acid to clear the solution.

Zinc.—Arsenic-free zinc shot, 3 to 6-in. mesh. The zinc is treated with C. P. hydrochloric acid, until the surface of the zinc becomes clean and dull. It is then washed, and kept, in a casserole, covered with distilled water, a clock-glass keeping out the dust.

[12] Prepared paper may be purchased from chemical dealers.

Mixed Acid.—One volume of arsenic-free H_2SO_4 is diluted with four volumes of pure water and to this are added 10 grams of NaCl per each 100 ml. of solution.

Stannous Chloride.—Eighty grams of stannous chloride dissolved in 100 ml. of water containing 5 ml. arsenic-free hydrochloric acid (1.2 sp.gr.).

Arsenic-free Hydrochloric Acid.—The commercial acid is treated with potassium chlorate to oxidize the arsenic to its higher form and the acid distilled.

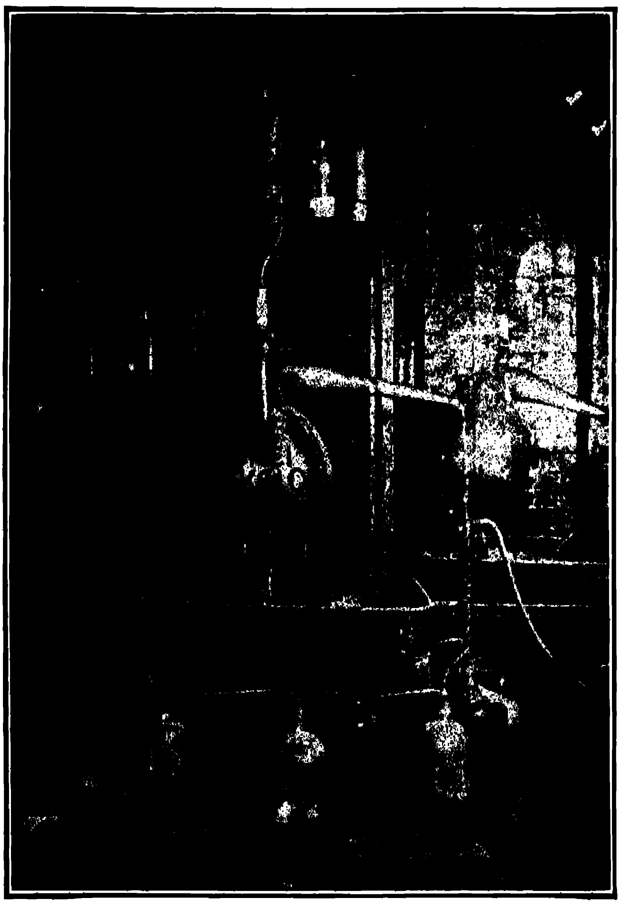


FIG. 13.—Purification of Hydrochloric Acid.

The distilling apparatus may be arrånged so that a constant distillation takes place, acid from a large container dropping slowly into a retort containing potassium chlorate, fresh hydrochloric acid being supplied as rapidly as the acid distills. See Fig. 13.

Lead Acetate Test Paper for Removal of H_2S.—Large sheets of qualitative filter paper are soaked in a dilute solution of lead acetate and dried. The paper is cut into strips 7×5 cm.

Blanks should be run on all reagents used for this work. The reagents are arsenic-free if no stain is produced on mercuric chloride paper after forty-five minutes' test.

Special Apparatus.—The illustration, Fig. 14, shows the Gutzeit apparatus connected up, ready for the test. The dimensions on the left-hand side are for the small apparatus and those on the right for the large form. Rubber stoppers connect the tubes to the bottle. The apparatus consists of a wide-mouth 2-oz. or 8-oz. bottle according to whether the small or large apparatus is desired, a glass tube (see Fig. 14) containing dry lead acetate paper and moist glass wool for removal of traces of hydrogen sulfide and a small-bore tube containing the strip of mercuric chloride paper.

PREPARATION OF THE SAMPLE

The initial treatment of the sample is of vital importance to the Gutzeit Method for determining traces of arsenic. The following procedures cover the more important materials or substances in which the chemist will be called upon to determine minute amounts of arsenic.

Traces of Arsenic in Acids.—The acid placed in the Gutzeit apparatus should be equivalent to 4.2 grams of sulfuric acid or 3.1 grams of hydrochloric acid and should contain 0.05 to 0.1 gram Fe_2O_3 equivalent. If large samples are required for obtaining the test it is necessary either to expel a portion of the acid in order to obtain the above acidity or to make standard stains under similar conditions of acidity. It must be remembered that arsenious chloride is readily volatile, whereas the arsenic chloride is not, hence it is necessary to oxidize arsenic before attempting to expel acids. If nitric acid or bromine or chlorine (chlorate) be added for this purpose, it must be expelled before attempting the Gutzeit test. Nitric acid may be expelled by adding sulfuric acid and taking to SO_3 fumes. Free chlorine, bromine, or iodine will volatilize on warming the solution. Chlorine in a chlorate is expelled by taking the sample to near dryness in presence of free acid. Sulfurous acid or hydrogen sulfide, if present, should be expelled by boiling the solution, then making faintly pink with $KMnO_4$ and destroying the excess with a drop or so of oxalic acid. SO_2 is reduced by zinc and hydrogen to H_2S, which forms black HgS with mercuric chloride, hence removal of SO_2 and H_2S are necessary before running the test.

Sulfuric Acid.—With amounts of arsenic exceeding 0.00005% As_2O_3, 5 to 10 grams of acid, according to its strength, are taken for analysis and diluted to 15 or 20 ml. If H_2S or SO_2 are present, expel by boiling for fifteen or twenty minutes. Prolonged fuming of concentrated acid should be avoided by previously diluting the acid with sufficient water. In mixed acid containing nitric acid the sample is taken to SO_3 fumes to expel nitric acid. The procedure given later for the regular determination is now followed.

For estimating very minute amounts of arsenic, 0.000005 to 0.00005% As_2O_3, it is necessary to take a 25- to 50-gram sample for analysis. The acid is treated as directed above for removal of H_2S or SO_2 or nitric acid and diluted in the Gutzeit apparatus to at least 130 ml., using the large apparatus. Add the iron and stannous chloride as directed in the procedure described on page 108 for large Gutzeit test. The stains are compared with standard stains

produced by known amounts of arsenic added to 50-gram portions of arsenic-free sulfuric acid of strength equal to that of the sample. The stains are longer and less intense than those produced by less acid.

Hydrochloric Acid.—Twenty ml. is taken for analysis (sp.gr. being known); the sample should contain an acid equivalent of about 3.1 grams of hydrochloric acid. Chlorine is expelled by bubbling air through the acid before taking a sample. The procedure is given for further treatment of the sample following the section on preparation of the sample.

Nitric Acid.—One hundred ml. of the acid (sp.gr. being known) is evaporated with 5 ml. of concentrated sulfuric acid to SO_3 fumes, to expel nitric acid. Arsenic is determined in the residue by the standard procedure.

Iron Ores, Pyrites, Burnt Pyrites, Cinders, etc.—One gram of the finely ground ore is oxidized by treating with 5 ml. of a mixture of 2 parts liquid bromine and 3 parts of carbon tetrachloride. After fifteen minutes, 10 ml. of concentrated nitric acid are added and the mixture taken to dryness. Five ml. of concentrated sulfuric acid (95%) are added and the mixture taken to SO_3 fumes to expel the nitric acid. The cooled sample is taken up with 50 ml. of water and digested until all of the iron sulfate has dissolved; it is now washed into a 100-ml. flask, made to volume, and arsenic determined in an aliquot portion in the usual way, given later. Insoluble Fe_2O_3, briquettes, etc., are best dissolved by fusion with potassium bisulfate, $KHSO_4$. The fused mass is dissolved in warm dilute hydrochloric acid, and then washed into the Gutzeit bottle.

Alumina Ores. Bauxite.—One gram of bauxite is treated with one part of concentrated nitric acid and 6 parts of concentrated hydrochloric acid, and taken to dryness on the water bath. The residue is taken up with an equivalent of 4.7 grams of hydrochloric acid or 6.3 grams of sulfuric acid in a volume of 25 ml. and the mix heated until the material has dissolved. The sample is diluted to exactly 100 ml. and arsenic determined on an aliquot portion.

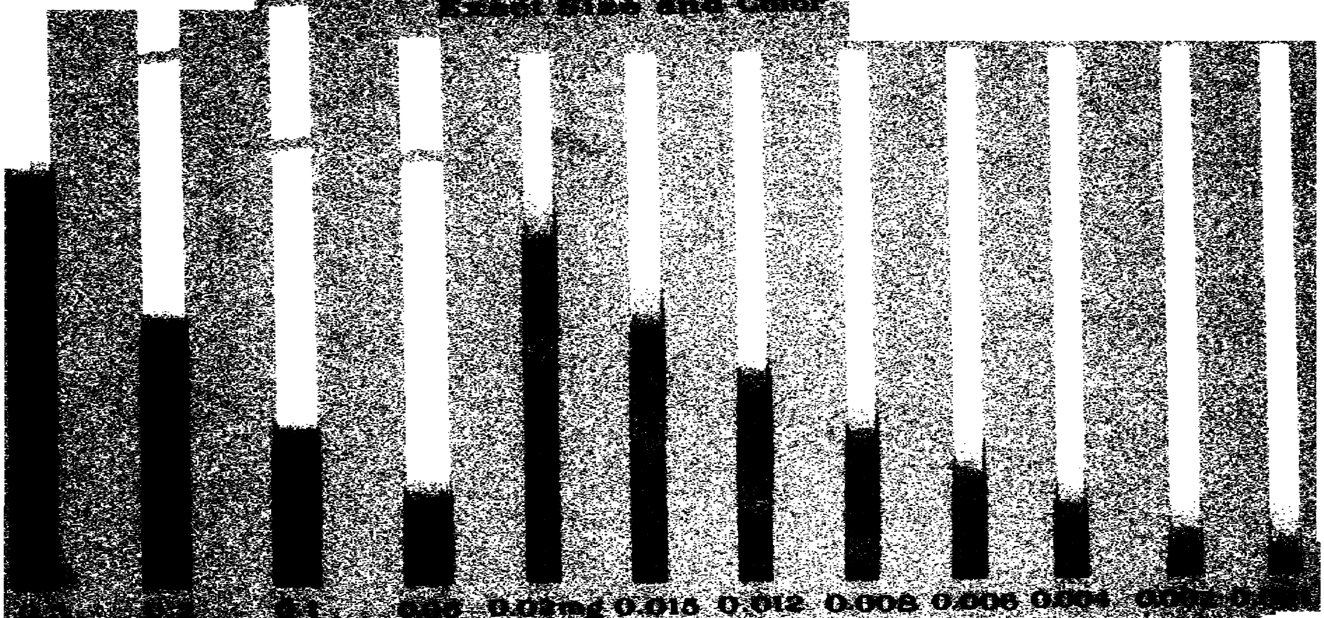
Phosphates, Phosphoric Acid.—Arsenic, in phosphoric acid, combined or free, cannot be determined in the usual way, as P_2O_5 has a retarding effect upon the evolution of arsine, so that the results are invariably low, small amounts of arsenic escaping detection. Arsenic, however, may be volatilized from phosphates and phosphoric acid, as arsenious chloride, $AsCl_3$, in a current of hydrogen chloride by heating to boiling. One gram or more of the phosphate is placed in a small distilling flask, connected directly to a 6-in. coil condenser dipping into the Gutzeit bottle, containing 20 to 30 ml. of cold distilled water. A second bottle connected in series may be attached for safeguarding loss (this seldom occurs). Fifty ml. of concentrated hydrochloric acid are added to the sample and 5 grams of cuprous chloride. Arsenic is distilled into the Gutzeit bottle by heating the solution to boiling and passing a current of air through strong hydrochloric acid into the distilling flask by applying suction at the receiving end of the system. All of the arsenic will be found in the first 10 or 15 ml. of the distillate. Arsenic may now be evolved after addition of iron, stannous chloride and zinc, as directed in the procedure.

Salts, Sodium Chloride, Magnesium Sulfate, etc.—One-gram samples are taken and dissolved in a little water and an equivalent of 6.3 grams of sulfuric acid added. The solution of iron and stannous chloride having been added, the run is made with 5 ml. of zinc shot, placed in the Gutzeit bottle.

Plate I

Arsenic Stains Gutzeit Method

Exact Size and Color



Large Gutzeit Apparatus   Small Gutzeit Apparatus

The numerals represent milligrams As_2O_3 causing the stain

Baking Powder, Other than Phosphate Baking Powder.—A 10-gram sample is heated with 10 ml. hydrochloric acid, 10 ml. of ferric ammonium alum and 30 ml. of distilled water, until the starch hydrolyzes. 0.5 ml. of stannous chloride is added to the hot solution and the mixture washed into the Gutzeit apparatus. The required amount of zinc is added and the arsenic determined as usual.

Phosphate Baking Powders.—Ten grams of the material mixed to a paste with about 50 ml. of hydrochloric acid are transferred to a small distilling flask with a few ml. of HCl. A tube, connected to a bottle of concentrated hydrochloric acid, passes into the mixture in the flask through a ground glass stopper. The flask is attached to a tube, which dips into water in a Gutzeit bottle. Two grams of cuprous chloride are added, the apparatus made tight and the flask immersed in boiling hot water. By aspirating air through the system into the Gutzeit bottle, which is water cooled, arsenic distills into the bottle and may be determined by the procedure outlined.

Arsenic in Organic Matter, Canned Goods, Meat, etc.—The finely chopped, well-mixed sample is placed in a large flask and enough water added to produce a fluid mass. An equal quantity of concentrated hydrochloric acid and 1 to 2 grams of potassium chlorate are added. The flask is shaken to mix the material and it is then placed on the steam bath. Upon becoming hot, nascent chlorine is evolved and vigorously attacks the organic matter. Half-gram portions of potassium chlorate are added at five-minute intervals, shaking the flask frequently. When the organic material has decomposed and the solution becomes a pale yellow color, the mass is diluted with water and filtered. Arsenic will be found in the filtrate. A white, amorphous substance generally remains on the filter, when cadaver is being examined. The filtrate is diluted to a given volume and an aliquot portion taken for analysis. This is evaporated to near dryness to expel excess of acid and decompose chlorates. An equivalent of 4.7 grams of hydrochloric acid is added (three times this amount for the large apparatus), the volume of the solution made to about 30 ml., 10 ml. of ferric ammonium alum and 0.5 ml. of stannous chloride added, and the solution poured into the Gutzeit apparatus for the test as follows.

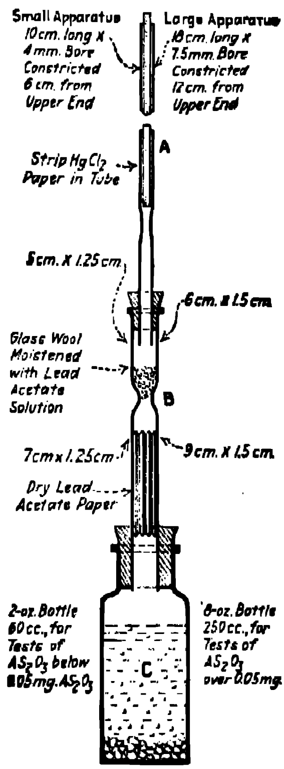


FIG. 14.—Gutzeit Apparatus for Arsenic Determination.

PROCEDURE FOR MAKING THE TEST

For amounts of arsenic varying from 0.001 milligram to 0.02 milligram As_2O_3, the small apparatus is used. The volume of the solution should be 50 ml. It should contain an equivalent of 4.2 to 6.3 grams sulfuric acid and should have about 0.1 gram equivalent of Fe_2O_3 reduced by 0.5 ml. of stannous chloride solution. Arsine is

generated by adding one 5-ml. crucible of arsenic-free zinc shot, $\frac{1}{3}$ to $\frac{1}{8}$-inch mesh. Temperature 75 to 80° F.

For amounts ranging from 0.02 to 0.5 milligram As_2O_3,[13] the large apparatus is used. The volume of the solution should be about 200 ml. and should contain an equivalent of 18.5 grams of sulfuric acid and should have 0.1 gram equivalent of Fe_2O_3, reduced by 0.5 ml. stannous chloride solution. Arsine is generated by adding one 12-ml. crucible of zinc shot ($\frac{1}{3}$ to $\frac{1}{6}$-inch mesh). The temperature should be 105° F. The sample taken should be of such size that a stain is obtained equivalent to that given by 0.1 to 0.5 milligram As_2O_3.

Lead acetate paper is placed in the lower portion of tube *B*; the upper portion of *B* contains glass wool moistened with lead acetate solution; the tube *A* contains the test strip of mercuric chloride paper. See Fig. 14. Immediately upon adding the required amount of zinc to the solution in the bottles, the connected tubes are put in position, as shown in the illustration, and the bottle gently shaken and allowed to stand for one hour for the small apparatus, forty minutes for the large. The test paper is removed, dipped in molten paraffine and compared with the standard stains. See Plate I.

Estimation of Per cent.

$$\frac{\text{The milligram } As_2O_3 \text{ stain} \times 100}{\text{Weight of sample taken}} =$$

References.—J. W. Burnes and C. W. Murray, "Accuracy of the Gutzeit Method for the Determination of Minute Quantities of Arsenic." Ind. Eng. Chem., Anal. Ed. **2**, 29, Jan. 1930.

"A Study of the Accuracy of the Gutzeit Method for Arsenic," J. R. Neller. J. Assoc. Official Agr. Chem., **12**, 332, 1929.

"History; Bibliography; Modifications," H. E. Crossley, J. Soc. Chem. Ind., **55**, 272T (1936).

"Sources of Error," W. Mühlsteph, Z. anal. Chem., **104**, 333 (1936).

"Preparation of Zinc Pellets of Uniform Size (Bullet mold)," P. L. Mills, J. Off. Agr. Chem., **18**, 506 (1935).

Review, G. Lockemann and B. F. v. Bülow, Z. anal. Chem., **94**, 322 (1933).

"Use of Diaphragm Instead of Paper Strips," C. E. Lachele, Ind. Eng. Chem., Anal. Ed. **6**, 256 (1934).

"Use of Tin Instead of Zinc to Prevent Evolution of SbH_3," N. A. Tananaev and V. D. Ponomarev, Z. anal. Chem., **101**, 183 (1935).

[13] It is advisable to use smaller samples when the arsenic content is over 0.3 milligram As_2O_3, as the longer stains are unreliable.

Ferrous iron prevents polarization between zinc and the acid and hence aids in the evolution of arsine.

In the analysis of baking powders, bauxite, sodium or similar salts, the distillation method is recommended. See page 107, "Phosphates," and "Phosphate baking powder."

Hydrochloric acid is used in place of sulfuric acid in cases where complete solution by the latter acid cannot be effected.

Standards and samples should be run under similar conditions, temperature, acidity, amount of zinc, volume of solution, etc. In place of zinc shot, zinc rods, cubes or discs may be used for generating arsine and hydrogen.

MARSH METHOD FOR ARSENIC

The famous Marsh test for arsenic is based on the reduction of As by nascent hydrogen. A flask containing a frothing mixture of arsenic-free zinc and sulfuric acid is connected with a glass tube constricted at two points. Through a funnel a solution of the suspected arsenic compound is added. The arsine formed by reduction is heated as it passes through the delivery tube and the element is deposited farther along as a shining mirror. It is best worked so that the mirror forms in a constriction. As little as one millionth of a gram of arsenic can be determined in this way, so the method has been used in poisoning cases. Description taken from "Holmes" General Chemistry.

The constricted part of the mirror tube is usually 1 mm. in width and the mirror of arsenic is compared with standard mirrors and thus determined quantitatively.

METHOD FOR ANALYSIS OF COMMERCIAL "ARSENIC," ARSENIOUS OXIDE, As_2O_3

The following constituents may be commonly present as impurities, SiO_2, Sb_2O_3, Fe_2O_3, NiO, CoO, CaO, SO_3, Cu, Pb, and Zn.

DETERMINATION OF MOISTURE

Two 10-gram samples are dried to constant weight in the oven at 100° C. Loss in weight = moisture.

SULFURIC ACID, H_2SO_4

The samples from the moisture determination are dissolved in concentrated hydrochloric acid, heating to boiling if necessary, and the samples diluted to 300 to 400 ml. Barium chloride solution is added in slight excess to the hot solution, the precipitate, $BaSO_4$, allowed to settle and filtered and the sulfate dried and ignited as usual.

$$BaSO_4 \times 0.343 = SO_3.$$

DETERMINATION OF ARSENIC AS As_2O_3

Duplicate 5-gram samples are dissolved in 20 grams potassium carbonate in 60 ml. of hot water, by boiling until solution is effected. The samples are

made up to 1 liter and aliquots of 100 ml. (=0.5 gram) taken for analysis. The solution is made faintly acid with hydrochloric acid, testing the solution with litmus paper or by adding methyl orange directly to the solution. An excess of bicarbonate is added and the arsenic titrated with tenth-normal iodine according to the standard procedure for arsenic. One ml. N/10 I = 0.004946 gram As_2O_3.

RESIDUE UPON SUBLIMATION OF As_2O_3. SiO_2, Pb, Cu, Fe_2O_3, NiO, CoO, Zn

Two 5-gram samples are weighed into tared porcelain crucibles and heated gently on sand baths with the sand banked carefully around the crucible so as to heat the entire receptacle. After the greater part of the arsenious oxide has volatilized, the crucible is ignited directly in the flame to a dull red heat, until fumes are no longer given off. The residue is weighed as total non-sublimable residue.

SILICA

The residues are transferred to beakers and treated with aqua regia, taken to dryness, and the silica dehydrated at 110° C. for an hour or more. The residue is taken up with hot dilute hydrochloric acid, boiled, and the silica filtered off, ignited, and weighed.

LEAD AND COPPER

The filtrate from the silica is "gassed" with H_2S and the precipitate filtered off. The filtrate is put aside for determination of iron, etc. The precipitate is dissolved in hot dilute nitric acid, 2 to 3 ml. of concentrated sulfuric acid added, the solution taken to SO_3 fumes, the cooled concentrate diluted to 20 or 30 ml., and the lead sulfate filtered off, ignited, and weighed as $PbSO_4$.

The filtrate from the lead sulfate containing the copper is treated with aluminum powder and the copper thrown out of solution; the excess of aluminum is dissolved with a few ml. of hydrochloric acid. The filtrate should be tested for copper with H_2S and the precipitate added to the copper thrown out by the aluminum. The copper on the filter is dissolved in hot dilute nitric acid, the extract evaporated to 2 or 3 ml., the acid neutralized with ammonia and then made acid with acetic, potassium iodide added and the liberated iodine titrated with standard thiosulfate solution according to the regular scheme for copper.

IRON, NICKEL, COBALT, AND ZINC

The filtrate from the H_2S Group is boiled to expel the H_2S and the iron oxidized by addition of nitric acid and boiling. The iron (and alumina) is precipitated with ammonium hydroxide and the precipitate filtered off and washed several times with hot water. If alumina is suspected (light-colored precipitate) it may be determined by the difference method—ignition of the precipitate, weighing, and finally subtracting the iron found by titration with standard stannous chloride solution. The iron is dissolved in hydrochloric acid and titrated hot with stannous chloride solution.

The filtrate from the iron is boiled and a 1% alcoholic solution of dimethylglyoxime added to precipitate the nickel. The salt is filtered on a tared Gooch, the precipitate dried at 100° C., and weighed. The weight of the salt$\times$0.2032 = Ni.

The filtrate from the nickel is boiled until all the alcohol has been driven off and the cobalt precipitated by addition of sodium hydroxide in excess, filtered, ignited, and weighed as Co_3O_4.

The filtrate is made acid with hydrochloric acid, and then alkaline with ammonium hydroxide and colorless sodium sulfide solution added to precipitate the zinc. The mixture is boiled five to ten minutes, the precipitated ZnS allowed to settle, filtered off, and washed once or twice and then dissolved in hydrochloric acid and the zinc determined by titration directly with potassium ferrocyanide, or by converting to the carbonate by addition of potassium carbonate, filtered and washed free of alkali, the precipitate dissolved in a known amount of standard acid, and the excess acid titrated with standard caustic (methyl orange indicator) according to the procedure given for zinc. $H_2SO_4 \times 0.6666 = Zn$.

ANTIMONY AND CALCIUM OXIDES

Two 15-gram samples are treated with 300 ml. of concentrated hydrochloric acid, boiled down to 50 ml. to expel the arsenic as $AsCl_3$, an equal amount of concentrated hydrochloric acid is added, and the last traces of arsenic precipitated by H_2S passed into the hot concentrated hydrochloric acid solution. The arsenious sulfide, As_2S_3, is filtered off. Antimony is precipitated by diluting the solution with an equal volume of water, the solution having been concentrated by boiling down to about 50 ml. The Sb_2S_3 is filtered off, washed several times with hot water, dissolved by washing through the filter with concentrated hydrochloric acid, and antimony determined in the strong hydrochloric acid solution by the potassium bromate method—addition of methyl orange indicator and titration with standard potassium bromate added to the hot solution to the disappearance of the pink color of the indicator.

The filtrate from the antimony is concentrated, made slightly alkaline with ammonium hydroxide, and gassed with hydrogen sulfide to remove iron, nickel, cobalt, zinc, chromium, and last traces of lead, etc. The filtrate is then concentrated and made acid with crystals of oxalic acid, boiled and methyl orange added and then ammonia drop by drop, slowly, until the indicator changes to an orange color. An excess of ammonium oxalate is now added and the beaker placed on the steam bath until the calcium oxalate has settled. The lime is now determined by filtering off the precipitate and washing, drying and igniting to CaO, or by titration with standard permanganate, according to the regular procedure for calcium.

ARSENIC IN IRON AND STEEL

Ten grams of sample are placed in a distillation flask and dissolved in dilute HNO_3, the solution evaporated to dryness and heated to expel oxides of nitrogen, 100 ml. of HCl and 20 grams of CuCl are added and the arsenious acid distilled and determined by the iodine method.

ARSENIC IN COPPER

Since arsenic impairs the electrical conductivity of copper, its determination is required. One gram of the sample is placed in a distillation flask with 10 ml. $FeCl_3$ and 100 ml. HCl and 5 grams KCl and the arsenious acid distilled and determined by titration with iodine.

DETERMINATION OF ARSENIC IN A WHITE ALLOY METAL[14]

(A) DETERMINATION WHERE ARSENIC EXCEEDS 0.05 PER CENT

Method.—Weigh 2–5 g. of sawings into a 250 ml. distilling flask having no side-arm, add at least 3 times as much $FeCl_3.6H_2O$ as sample weighed out, about 2 g. of KCl, and 100–150 ml. of HCl (sp.gr. 1.19). Connect up with a condenser and distill into 100 ml. of cold distilled water[15] having the lower end of the condenser immersed in the water. Distill down to a volume of about 30 ml.[16] or until the solution begins to bump due to the separation of $PbCl_2$. Wash down the condenser, set a beaker of fresh water under the condenser, add 50 ml. of HCl (sp.gr. 1.19) to the solution in the flask and distill as before. Wash down condenser.

[14] Standard Method of the National Lead Company—by courtesy of the Company through kindness of W. A. Brown.

[15] The distillate should be kept cold by setting the beaker in a large sized casserole and packing around it with cracked ice.

[16] If the alloy is high in antimony and the solution is taken too low, antimony will distill over.

Pass H_2S through both solutions for 45 minutes. If As_2S_3 appears to precipitate in the second solution make a third distillation. After passing H_2S through the distillates, allow them to stand in a warm place for several hours, again pass H_2S for 15 minutes and filter them through a previously prepared Gooch[17] crucible, washing first with hot distilled water and once with 95% alcohol. Now cut off the suction, add 10 ml. of CS_2, allow it to drain through and then connect up with the suction again until the pad is apparently dry; repeat with 5 ml. of CS_2. Dry at 105° C. for 30 minutes, cool and weigh. Dissolve the As_2S_3 on the pad, first with a half saturated solution of $(NH_4)_2CO_3$ and then with NH_4OH (1 : 2); wash several times with hot distilled water and once with 95 per cent alcohol. Dry as before, cool and weigh. The loss in weight is As_2S_3. Calculate to As.

Run in duplicate.

(B) DETERMINATION WHERE ARSENIC IS LESS THAN 0.05 PER CENT

Weigh 10–30 g. of sawings into a 1000-ml. wash bottle flask, add at least 3 times as much ferric chloride as sample present and about 400 ml. of HCl (sp.gr. 1.19). Distill as in method (*a*) until the solution begins to bump. Wash down the condenser. Transfer the clear solution to another 1000-ml. flask, add about 50 ml. of hot water and combine the dissolved lead chloride solution with the decanted solution in the second flask. To the original flask add about 10 g. of ferric chloride, 2 g. of KCl and about 100 ml. of HCl (sp.gr. 1.19), connect up both flasks with condensers, set a beaker of fresh water under each condenser and redistill. When the distillation is finished wash down the condenser and pass H_2S through all 3 solutions as in method (*a*). If a precipitate of As_2S_3 appears in the last two distillates, distill again. Proceed as described in method (*a*).

Run in duplicate.

[17] To prepare the Gooch crucible, first introduce a disc of filter paper that will snugly fit the bottom of the crucible, then add the asbestos, wash with distilled water and once with 95 per cent alcohol. Dry at 105° C. for 30 minutes, cool and weigh.

DETERMINATION OF ARSENIC AND ANTIMONY IN A WHITE METAL ALLOY

STIEF METHOD[18]

Apparatus.—A condenser is made of glass tubing in the form of a letter S, about 18″ long and ½″ inside diameter, tapering to about ¼″ at the upper end and to about ⅛″ at the lower end. One curve is nearly filled with water, and is submerged in cold water in a 500-ml. beaker. The lower end dips into about 75 ml. of water in a 300-ml. beaker and the upper end is connected by a delivery tube with a 300-ml. Florence flask, closed with a rubber stopper which is fitted with a delivery tube and with a thermometer reaching to about 1″ above the surface of the liquid in the flask.

Solutions Required. ***Potassium Permanganate*** (*N/10*).—Dissolve 3.16 of $KMnO_4$ in about 500 ml. of distilled water and allow to stand several days. Filter off, without washing, through glass wool, into a 100-ml. graduated flask, make up to mark and mix thoroughly. Standardize against Bureau of Standards' sodium oxalate by accurately weighing 0.25 g.–0.30 g. of $Na_2C_2O_4$, brush into a 300-ml. beaker, dissolve with 200 ml. of hot water, add 20 ml. H_2SO_4 (1 : 1) and titrate with $KMnO_4$ solution to the first tinge of a permanent pink. Calculate[19] to antimony; each ml. is equivalent to approximately 0.006 g. of antimony. Also standardize against a white metal alloy of known antimony content having exactly the same conditions for titration as are specified for the analysis of the sample.

Starch Solution.—See " Determination of Tin in a White Metal Alloy."

Method. (*a*) *Determination of Arsenic.*—Weigh 1.0 g. of sawings, brush into a 300 ml. Florence flask, add 15 ml. H_2SO_4 (sp.gr. = 1.84) and heat on the hot plate until completely dissolved. Cool, add 15 ml. of water and a bulk of 0.5 ml. of pumice stone,[20] and boil gently for about 5 minutes or until the strong odor of SO_2 can no longer be detected. Cool, cautiously add 25 ml. HCl (sp.gr. = 1.18), insert the stopper carrying the delivery tube and thermometer and connect the delivery tube with the " S " condenser. Heat the solution to gentle boiling for from 10 to 15 minutes, keeping the vapor temperature[21] at 107° C. for at least 5 minutes. Wash the contents of the condenser into a 300-ml. beaker; neutralize with $NaHCO_3$; add 2 g. $NaHCO_3$ in excess, dilute to

[18] Stief, J. Ind. Eng. Chem., 7, 211 (1915); see also A.S.T.M., "The Chemical Analysis of Metals," pp. 190–192 (1936).

[19] 1 ml. $N/10\ KMnO_4 = 1$ ml. $N/10\ Na_2C_2O_4 = 0.0067$ g. $Na_2C_2O_4$,

$$1 \text{ ml. } N/10\ KMnO_4 = \frac{\text{Atomic Weight Sb}}{2 \times 1000} = 0.006088 \text{ g. Sb.}$$

Should B g. of $Na_2C_2O_4$ require b ml. of $KMnO_4$, then

$$1 \text{ ml. } KMnO_4 = B/b \text{ g. } Na_2C_2O_4$$

$$= B/b \times \frac{6.088}{67.0} \text{ g. Sb.}$$

[20] The pumice stone used for this purpose should be of such size as to pass through a 10 mesh but not a 20 mesh sieve.

[21] Should the temperature get above 107° C. there is danger of a loss of antimony.

a volume of 200 ml. with water at room temperature, add 2 ml. of starch solution and titrate with N/10 iodine [22] to the first tinge of permanent blue. Deduct 0.1 ml. as a correction for a blank and calculate for arsenic content.

(*b*) *Determination of Antimony.*—Wash the stopper and thermometer with cold distilled water, combine washings with main solution, dilute to a volume of 200 ml., add 10 ml. of HCl (sp.gr. = 1.18), cool in tap water and titrate with N/10 $KMnO_4$ to the first permanent tinge of pink. Deduct 0.1 ml. as a correction for a blank.

OTHER METHODS FOR DETERMINATION OF ARSENIC

A SIMPLE METHOD OF THE DETERMINATION OF ARSENIC IN SMALL QUANTITIES OF ORGANIC SUBSTANCE [23]

The method depends upon the fact that during the destruction of the organic substance As is oxidized to arsenate; this liberates I from KI which can be titrated with $Na_2S_2O_3$.

Procedure.—Boil 7–12 mg. of the substance with 1 ml. of 30% H_2SO_4 and a few drops of concentrated HNO_3, add more HNO_3 and boil longer, evaporate several times with addition of a few drops of perhydrol, dissolve in 1 ml. of water, evaporate until SO_3 is evolved, repeat this process, add 1 ml. of water, boil out of contact of air, add fresh concentrated HCl and 2 ml. of 4% KI solution (free of iodates), let stand closed for 10 minutes and titrate the I with 0.01 N $Na_2S_2O_3$. If the solution is only pale yellow, make it up to 20 ml., add 5 drops of 1% starch solution, and titrate to the appearance of a characteristic pale reddish end point. When halogens are present in the organic substance special precautionary measures are necessary to obtain correct results. The

[22] The iodine solution is standardized by measuring off 25 ml. into a 300-ml. flask, dilute to 150 ml. with cold distilled water, titrate with standard $Na_2S_2O_3$ solution, to a pale straw color, add 2 ml. of starch solution, and continue the titration to the disappearance of the blue color. The $Na_2S_2O_3$ solution should be an approximately N/10 solution and is standardized in terms of Sb. The method of calculating the strength of the iodine in terms of arsenic can best be shown by the following example:

Let

$$1 \text{ ml. } Na_2S_2O_3 \text{ solution} = 0.006 \text{ g. Sb}$$

and let

$$25 \text{ ml. iodine solution} = 25.5 \text{ ml. } Na_2S_2O_3 \text{ solution.}$$

Then

$$1 \text{ ml. iodine solution} = \left(0.006 \times \frac{25.5}{25} \times \frac{37.49}{60.88}\right) \text{ g. of arsenic.}$$

[23] O. Wintersteiner and H. Hannel, Mikrochemie, **4**, 155–67; also Chem. Zentr., **11**, 3065, 1926. C. A., **22**, 3369, 1928.

method gives reliable results, and is particularly serviceable in elementary organic analysis.

METHOD FOR THE COLORIMETRIC DETERMINATION OF ARSENIC[24]

The method depends upon Feigl's test for As with a few drops of cold saturated solution of $(NH_4)_2MoO_4$ followed by an excess of $SnCl_2$ solution in HCl. A blue color develops which disappears on heating in the absence of As but remains in its presence, the intensity of the color being proportional to the amount. The reaction has a sensitivity of 1 : 1,000,000. When the quantity of As is very small the blue color may be completely masked by the brown reduction products of Mo and it is recommended to extract the blue color with MeOH.

For making the determination in serum or urine a preliminary ashing of the sample is necessary. This is best done with the aid of aqua regia in a crucible (1 ml. of aqua regia for 2 ml. serum), the contents being evaporated to dryness and this is repeated several times. The residue is finally taken up in phosphate, the As being precipitated from the solution by reduction with NaH_2PO_2 according to the equation:

$$As_2O_3 + 3H_3PO_2 = 3H_3PO_3 + 2As.$$

One volume of the solution is treated with 3 volumes of the reagent, which is prepared by dissolving 1 part $NaH_2PO_2 \cdot H_2O$ in 10 parts of 25% HCl, and heating this on a water bath. The precipitate is collected on a paper or asbestos filter and washed with cold water. The precipitate is dissolved in perhydrol (H_2O_2), the solution is evaporated to dryness, taken up in H_2O and the color reaction is accomplished as explained before. On boiling, the blue color is replaced by a greenish brown, but is extracted by shaking with 3 ml. MeOH and the color is matched against that produced by a standard As_2O_3 solution.

[24] A. Polyakov and N. Kolokolov, Biochem. Z., **213**, 375–9, 1929. C. A., **24**, 311, 1930.

BARIUM[1]

Ba, ***at.wt.*** **137.36;** ***sp.gr.*** **3.78;** ***m.p.*** **850° C.;** ***volatile at*** **950° C.;** ***oxides,*** **BaO, BaO_2**

Barium occurs combined in nature as sulfate, $BaSO_4$, barite or heavy spar; as carbonate, $BaCO_3$, witherite, and as baryto-calcite, $BaCO_3 . CaCO_3$. It occurs in feldspatic rocks, commonly associated with strontium, and in minute quantities (less than 0.2%) in many of the silicate rocks. Barium is never found free in nature.

DETECTION

Barium is precipitated as the carbonate together with strontium and calcium, by addition of ammonium hydroxide and ammonium carbonate to the filtrate of the ammonium sulfide group. It is separated from strontium and calcium by precipitation as yellow barium chromate, $BaCrO_4$, from a dilute acetic acid solution.

Saturated solutions of calcium or strontium sulfate precipitate white barium sulfate, $BaSO_4$, from a chloride or nitrate or acetate solution, barium sulfate being the least soluble of the alkaline earth sulfates.

Soluble chromates precipitate yellow barium chromate from a neutral or dilute acetic acid solution, insoluble in water, moderately soluble in chromic acid, soluble in hydrochloric or nitric acid.

Fluosilicic acid, H_2SiF_6, precipitates white, crystalline barium fluosilicate, $BaSiF_6$, sparingly soluble in acetic acid, insoluble in alcohol. (The fluosilicates of calcium and strontium are soluble.)

Flame.—Barium compounds color the flame yellowish green, which appears blue through green glass.

Spectrum.—Three characteristic green bands (α, β, γ).

[1] Barite was investigated by V. Casciorolus, a shoemaker of Bologna, in 1602, who found that the material became phosphorescent upon ignition with a combustible material (Bolognian phosphorus). Scheele found heavy spar in pyrites in 1774. The discovery of the metal was accomplished by Sir Humphry Davy, by electrolysis of the chloride in presence of mercury (1808).

Metallic barium is used as a lining in photo-electric cells and in amplification tubes. The oxide was formerly used in preparing oxygen, and the peroxide in making hydrogen peroxide. The sulfide is used in luminous paint and as a depilatory, the chromate is used as a paint pigment, the sulfate in medical X-ray work, and in lithopone. The oxide has been proposed for sugar refining and as a substitute for calcium in sulfur insecticides.

Barium sulfate is precipitated by addition of a soluble sulfate to a solution of a barium salt. The compound is extremely insoluble in water and in dilute acids (soluble in hot concentrated sulfuric acid). The sulfate is readily distinguished from lead sulfate by the fact that the latter is soluble in ammonium salts, whereas barium sulfate is practically insoluble.

Microscopical Examination.—G. Deniges (Compt rend., **170**, 996–9, 1920) gives a technic for testing for the alkaline earths with 10% solution of HIO_3. The salt is pulverized, a drop of water added and then a minute drop of the HIO_3 reagent. The microscope reveals pointed octahedra for Ca, shorter octahedra and rhombic prisms with high refraction for Sr, and needle prisms grouped in clusters for Ba.

ESTIMATION

The determination of barium is required in the valuation of its ores, barite, heavy spar, $BaSO_4$; witherite, $BaCO_3$; baryto-calcite, $BaCO_3.CaCO_3$. It is determined in certain white mixed paints and colored pigments, Venetian, Hamburg or Dutch whites, chrome paints, etc., in analysis of Paris green, baryta insecticides, putty, asphalt, dressings and pavement surfacings. It may be found as an adulterant in foods, wood preservatives, filler in rubber, rope, fabrics. It is determined in salts of barium. The nitrate is used in pyrotechny, in mixtures for green fire.

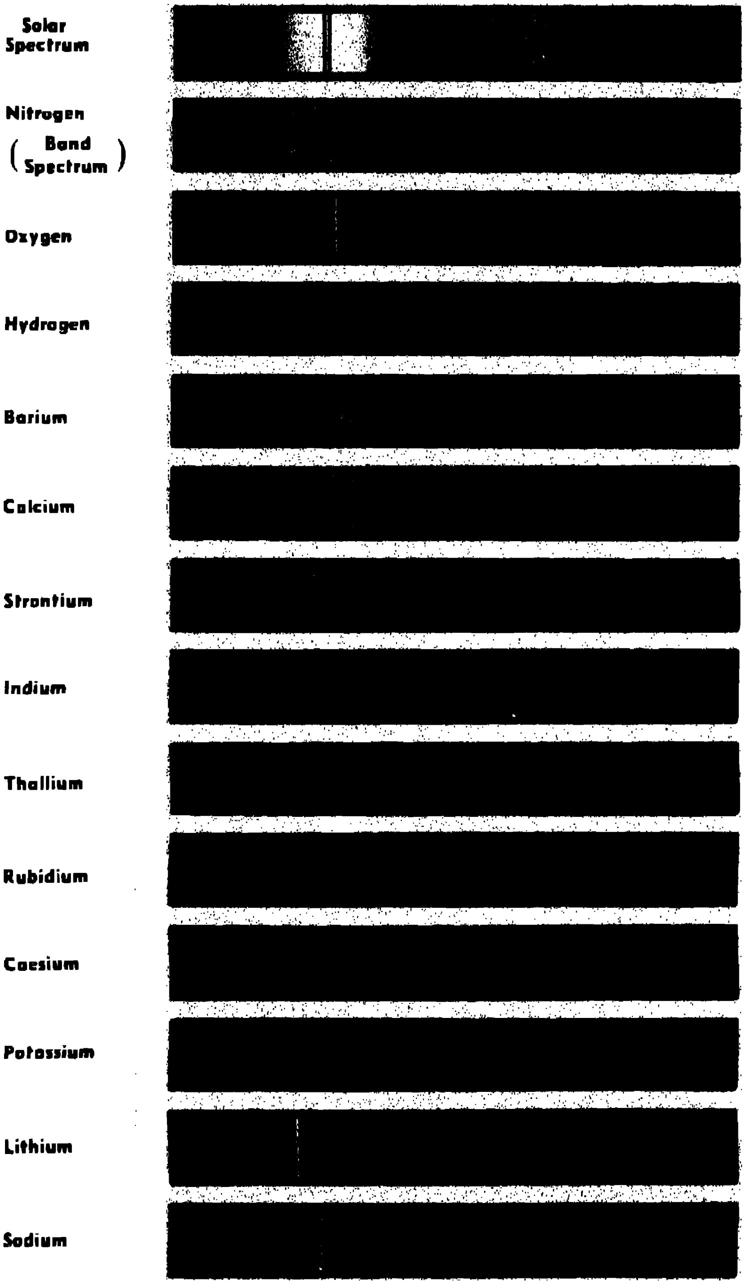
The formation of water soluble chlorides is desired in the decomposition of the material. This is accomplished by the action of HCl followed by Na_2CO_3 fusion of the acid insoluble material with subsequent water extraction and final solution of the water insoluble carbonate with HCl. In presence of phosphates, fluorides or carbonates the alkaline earth group (Ba, Ca, Sr) will precipitate with iron and alumina.

PREPARATION AND SOLUTION OF THE SAMPLE

Compounds of barium, with the exception of the sulfate, $BaSO_4$, are soluble in hydrochloric and nitric acids. The sulfate is soluble in hot concentrated sulfuric acid, but is reprecipitated upon dilution of the solution. The sulfate is best fused with sodium carbonate, which transposes the compound to barium carbonate; sodium sulfate may now be leached out with water and the residue, $BaCO_3$, then dissolved in hydrochloric acid.

Solution of Ores. Sulfates.—0.5 to 1 gram of the finely divided ore is fused with 3 to 5 grams of sodium and potassium carbonate mix, 2 : 1, or sodium carbonate alone, in a platinum dish. (Prolonged fusion is not neces-

EMMISSIONS - SPECTRA



sary.) The melt is cooled and then extracted with hot water to dissolve out the alkali sulfates. Barium carbonate, together with the other insoluble carbonates, may now be dissolved by hot dilute hydrochloric acid. From this solution barium may be precipitated by addition of sulfuric acid. If it is desired to separate barium along with strontium, calcium, and magnesium, the members of the preceding groups are removed by H_2S in acid and in ammoniacal solution, as directed under "Separations."

Sulfides.—The ore is oxidized, as directed for pyrites under the subject of sulfur. After the removal of the soluble sulfates, the residue, containing silica, barium, and small amounts of insoluble oxides, is fused and dissolved according to the procedure for sulfates.

Carbonates.—In absence of sulfates the material may be dissolved with hydrochloric acid, taken to dryness to dehydrate silica and after heating for an hour in the steam oven (110° C.) the residue is extracted with dilute hydrochloric acid and filtered. The filtrate is examined for barium according to one of the procedures given later.

Salts Soluble in Water.—Nitrates, chlorides, acetates, etc., are dissolved with water slightly acidulated with hydrochloric acid.

Material Containing Organic Matter.—The substance is roasted to destroy organic matter before treatment with acids or by fusion with the alkali carbonates.

The Insoluble Residue remaining from the acid treatment of an ore may contain barium sulfate in addition to silica, etc. The filter containing this residue is burned and the ash weighed. Silica is now volatilized by addition of hydrofluoric acid with a few drops of sulfuric acid, and evaporation to dryness. If an insoluble substance still remains after taking up the remaining residue with dilute hydrochloric acid, barium sulfate is indicated. This is treated according to the method given for sulfates.

Note.—The insoluble substance remaining is frequently ignited and weighed as barium sulfate without fusion with the carbonate.

SEPARATIONS

The Alkaline Earths

Preliminary Considerations.—In the determination of barium, calcium, and strontium, the following causes may lead to loss of the elements sought:

a Presence of Phosphates—Phosphoric acid, free or combined, has a decided influence upon the determination of the members of this group. Combined as phosphate it will cause the complete precipitation of barium, calcium, and strontium, along with iron, alumina, etc., upon making the solution [illegible] for removal of the ammonium sulfide group. It is a common practice to hold up the iron+alumina by means of tartaric, citric, or other organic acid, before making ammoniacal for precipitation of this group as oxalates, or the basic acetate method is used for precipitation of iron and alumina; [illegible] barium, and strontium going into solution. These procedures may be satisfactory for the analysis of phosphate rock and similar products, but do [illegible] with the difficulty when large amounts of phosphates are present. In [illegible] containing free phosphoric acid, barium, calcium, and strontium, [illegible]

small amounts, may remain in solution in presence of sulfates or oxalates. Appreciable amounts of calcium, 1% or more, may escape detection by the usual method of precipitation by ammonium oxalate added to the alkaline solution, on account of this interference, so that the removal of phosphoric acid before precipitation of this group is frequently necessary. This may be accomplished by addition of potassium carbonate in sufficient excess to combine completely with the phosphoric acid and form carbonates with the bases. The material taken to dryness is fused with additional potassium carbonate in an iron crucible, and the fusion leached with hot water—sodium phosphate dissolves and the carbonates of the heavy metals remain insoluble.

b. Another source of loss is the presence of sulfates, either in the original material or by intentional or accidental addition, in the latter case due to the oxidation of hydrogen sulfide, which has been passed into the solution during the removal of elements of the hydrogen sulfide and ammonium sulfide groups, barium and strontium sulfate being precipitated along with these members. A potassium carbonate fusion will form K_2SO_4, which may be leached out with water.

c. Loss may be caused by occlusion of barium, calcium, strontium, and magnesium by the gelatinous precipitates $Fe(OH)_3$, $Al(OH)_3$, etc. A double precipitation of these compounds should be made if considerable amounts are present.

d. A large excess of ammonium salts, which accumulate during the preliminary separations, will prevent precipitation of the alkaline earths. This can be avoided by using the necessary care required for accurate work, the addition of reagents by means of burettes or according to definite measurements in graduates, etc. Careless addition of large amounts of ammonium hydroxide and hydrochloric acid should be guarded against. In case large amounts of ammonium chloride are present, time is frequently saved by a repetition of the separations. Ammonium chloride may be expelled by heating the material, taken to dryness in a large platinum dish, the ammonium salts being volatilized.

e. Carbon dioxide absorbed by ammonium hydroxide from the air will precipitate the alkaline earths with the ammonium sulfide group.

Direct Precipitation on Original Sample.—For the determination of barium, calcium, and strontium, it is advisable to take a fresh sample, rather than one that has been previously employed for the estimation of the hydrogen sulfide and ammonium sulfide groups, as is evident from the statements made above. The alkaline earths are isolated by being converted to the insoluble sulfates and separations effected as given later under Sulfate Method.

Preliminary Tests.—Much time may be saved by making a preliminary test for barium, strontium, and calcium by means of the spectroscope and avoiding unnecessary separations.

By means of the spectroscope with the use of the ordinary Bunsen flame exceedingly minute amounts of calcium, strontium and barium may be detected per ml. The test is very much more delicate by the arc spectra method.[1a] The liquid containing the substance is connected to the positive pole and an iridium needle is connected by means of an adjustable resistance of 300 to 500 ohms to the negative pole. An E.M.F. of 100 to 200 volts and 1 ampere

[1a] E. H. Riesenfeld and G. Pfützer, Ber., **46**, 3140–3144, 1913; Analyst, **38**, 584, 1913.

current are required. By the arc it is possible to detect 0.002 milligram of calcium, 0.003 milligram of strontium, 0.006 milligram of barium, 0.1 milligram of magnesium per ml. In these concentrations, calcium shows one brilliant line (423 $\mu\mu$), a bright line (616 $\mu\mu$), and a faint line between them; strontium two bright lines (422 and 461 $\mu\mu$) and two fairly bright lines; barium two brilliant lines (455 and 493 $\mu\mu$), two other bright lines, and a fairly bright one; and magnesium a brilliant band composed of three lines (516.8 to 518.4 $\mu\mu$), as well as a fairly bright line further towards the violet end of the spectrum.

The flame test may be of value in absence of sodium; barium giving a green flame, strontium a brilliant scarlet, and calcium an orange red.

Separation of the Alkaline Earths from Magnesium and the Alkalies.—Two general procedures will cover conditions commonly met with in analytical work:

A. Oxalate Method.—Applicable in presence of comparatively large portions of calcium. The acid solution containing not over 1 gram of the mixed oxides is brought to a volume of 350 ml. and for every 0.1 gram of magnesium present about 1 gram of ammonium chloride is added, unless already present. Sufficient oxalic acid is added to completely precipitate the barium, calcium, and strontium.[2] ($H_2C_2O_4.2H_2O = 126.07$, $Ba = 137.36$, $Ca = 40.08$, $Sr = 87.63$.) The solution is slowly neutralized by addition, drop by drop, of dilute ammonium hydroxide (1 : 10), methyl orange being used as indicator. About ½ gram of oxalic acid is now added in excess, the solution again made alkaline with ammonium hydroxide, and allowed to settle for at least two hours. The precipitate is filtered off and washed with water containing 1% ammonium oxalate, faintly alkaline with ammonia.

The precipitate contains all the calcium and practically all the barium and strontium. If Mg is present in amounts of 10 to 15 times that of the alkaline earths a double precipitation is necessary to remove it completely from this group. The oxalates are dissolved in hydrochloric acid and reprecipitated with ammonium oxalate in alkaline solution.

The filtrate contains magnesium and the alkalies. Traces of barium and strontium may be present. If the sample contains a comparatively large proportion of barium and strontium, the filtrate is evaporated to dryness, the ammonium salts expelled by gentle ignition of the residue, and the Ba and Sr recovered as sulfates according to the method described below. Magnesium is precipitated as magnesium ammonium phosphate from the filtrate.

The oxalates of barium, calcium, and strontium are ignited to oxides, in which form they may be readily converted to chlorides by dissolving in hydrochloric acid, or to nitrates by nitric acid.

B. Sulfate Method.—Applicable in presence of comparatively large proportions of barium, strontium, or magnesium. The solution containing the alkaline earths, magnesium and the alkalies is evaporated to dryness and about 5 ml. concentrated sulfuric acid added, followed by 50 ml. of 95% alcohol. The sulfates[3] of barium, calcium, and strontium, are allowed to settle, and then filtered on to a fine grained ashless filter paper and washed

[2] Calcium and strontium will slowly precipitate in the oxalic acid solution. Ba oxalate will precipitate upon making the solution alkaline.

[3] Solubility of $BaSO_4 = 0.17$ milligram, $CaSO_4 = 179$ milligram, $SrSO_4 = 11.4$ milligrams per 100 ml.

with alcohol until free of magnesium sulfate. In presence of large amounts of magnesium as in case of analyses of Epsom salts and other magnesium salts it will be necessary to extract the precipitate by adding a small amount of water, then sufficient 95% alcohol to make the solution contain 50% alcohol and filter from the residue. Magnesium is determined in the filtrate.

The residue containing barium, calcium, and strontium as sulfate is fused with 10 parts of potassium carbonate or sodium acid carbonate until the fusion becomes a clear molten mass, a deep platinum crucible being used for the fusion. A platinum wire is inserted and the mass allowed to solidify. The fusion may be removed by again heating until it begins to melt around the surface next to the crucible, when it may be lifted out on the wire. The mass is extracted with hot water and filtered, Na_2SO_4 going into the solution and the carbonates of barium, strontium, and calcium remaining insoluble. The carbonates should dissolve completely in hydrochloric acid or nitric acid, otherwise the decomposition has not been complete, and a second fusion of this insoluble residue will be necessary.

Separation of the Alkaline Earths from One Another.—This separation may be effected by either of the following processes:

1. Barium is separated in acetic acid solution as a chromate from strontium and calcium; strontium is separated as a nitrate [4] from calcium in ether-alcohol or amyl alcohol.

2. The three nitrates are treated with ether-alcohol in which barium and strontium nitrates are insoluble and calcium dissolves; the barium is now separated from strontium by ammonium chromate.

Procedures. 1. (a) Separation of Barium from Strontium (and from Calcium).—In presence of an excess of ammonium chromate, barium is precipitated from solutions, slightly acid with acetic acid, as barium chromate (appreciably soluble in free acetic acid), whereas strontium and calcium remain in solution.

The mixed oxides or carbonates are dissolved in the least amount of dilute hydrochloric acid and the excess of acid expelled by evaporation to near dryness. The residue is taken up in about 300 ml. of water and 5–6 drops of acetic acid (sp.gr. 1.065) together with sufficient ammonium acetate (30% solution) to neutralize any free mineral acid present. The solution is heated and an excess of ammonium chromate (10% neutral soln.) [5] added (10 ml. usually sufficient). The precipitate of barium chromate is allowed to settle for an hour and filtered off on a small filter and washed with water containing ammonium chromate until free of soluble strontium and calcium (test—addition of NH_4OH and $(NH_4)_2CO_3$ produces no cloudiness), and then with water until practically free of ammonium chromate (e.g., only slight reddish brown color with silver nitrate solution).

To separate any occluded precipitate of strontium or calcium the filter paper is pierced and the precipitate rinsed into a beaker with warm dilute nitric acid (sp.gr. 1.20) (2 ml. usually are sufficient). The solution is diluted to about 200 ml. and boiled. About 5 ml. of ammonium acetate, or enough to neutralize the free HNO_3, are added to the hot solution and then sufficient ammonium

[4] Method of Stromayer and Rose. H. Rose, Pogg. Ann., 110, 292, 1860.

[5] The solution is prepared by adding NH_4OH to a solution of $(NH_4)_2Cr_2O_7$ until yellow. The solution should be left acid rather than alkaline.

chromate to neutralize the free acetic acid, 10 ml. usually being sufficient. The washing, as above indicated, is repeated. Barium is completely precipitated and may be determined either as a chromate or a sulfate or by a volumetric procedure. Strontium and calcium are in the filtrates and may be separated as follows:

(b) Separation of Strontium from Calcium.—The method depends upon the insolubility of strontium nitrate and the solubility of calcium nitrate in a mixture of ether-alcohol, 1 : 1.

Solubility of $Sr(NO_3)_2$ = 1 part $Sr(NO_3)_2$ in 60,000 parts of the mixture. Ca easily soluble. According to Fresenius [6] 0.0023 g. $Sr(NO_3)_2$ per 250 ml. and 0.37 g. $Ca(NO_3)_2$ per 1 ml.

If the solution is a filtrate from barium, 1 ml. of nitric acid is added and the solution heated and made alkaline with ammonium hydroxide followed immediately with ammonium carbonate, the carbonates of strontium (together with some $SrCrO_4$) and calcium will precipitate. The precipitate is dissolved in hydrochloric acid and reprecipitated from a hot solution with ammonium hydroxide and ammonium carbonate. The precipitate, $SrCO_3$ and $CaCO_3$, is washed once with hot water and is then dissolved in the least amount of nitric acid, washed into a small casserole, evaporated to dryness and heated for an hour at 140 to 160° C. in an oven, or at 110° C. over night. The dry mass is pulverized and mixed with 10 ml. of ether-alcohol (absolute alcohol, one part, ether-anhydrous, one part). Several extractions are thus made, the extracts being decanted off into a flask. The residue is again dried in an oven at 140 to 160° C., then pulverized and washed into the flask with the ether-alcohol mixture and digested for several hours with frequent shaking of the flask. The residue is washed on to a filter moistened with ether-alcohol mixture. Strontium nitrate, $Sr(NO_3)_2$, remains insoluble, and may be dissolved in water and determined gravimetrically as a sulfate, oxide, or carbonate or volumetrically. Calcium is in the filtrate and may be determined gravimetrically as an oxide or volumetrically.

Instead of using a mixture of ether-alcohol, amyl alcohol may be used (hood), the mixture being kept at boiling temperature to dehydrate the alcohol to prevent solution of strontium (*b.p.* = 130° C.).

2. Separation of Barium and Strontium from Calcium.[7]—The procedure depends upon the insolubility of barium nitrate, $Ba(NO_3)_2$, and strontium nitrate, $Sr(NO_3)_2$, in a mixture of anhydrous ether and absolute alcohol or anhydrous amyl alcohol, whereas $Ca(NO_3)_2$ dissolves.

The mixed oxides or carbonates are dissolved in nitric acid and taken to dryness in a beaker or Erlenmeyer flask, and heated for an hour or more in an oven at 140 to 160° C. Upon cooling, the mixture is treated with ten times its weight of ether-alcohol mixture and digested, cold, in a covered beaker or corked flask for about two hours with frequent stirring. An equal volume of ether is now added and the digestion continued for several hours longer. The residue is washed by decantation with ether and alcohol mixture until calcium is removed (test—no residue on platinum foil with drop of filtrate evaporated to dryness).

[6] Z. anal. Chem., **32**, 189, 1893.
[7] See Fresenius, Z. anal. Chem., **29**, 413–430, 1890.

Separation of Barium from Strontium.—The dry mixed chlorides are dissolved in the least possible amount of water (0.2 ml., or more if necessary) the solution warmed, then cooled. More water is added if crystals appear. (The solution should be saturated.) A mixture of 4 : 1 of HCl (33%) and ether is added dropwise with stirring. Sufficient reagent is added to precipitate $BaCl_2$ and dissolve $SrCl_2$. The mixture is decanted on an asbestos filter and washed with the HCl-ether reagent. The $BaCl_2$ is dried at 150° C. and weighed. (Method of Gooch and Soderman.)

Barium and strontium may be separated by precipitation of barium as a chromate, the nitrate residue being dissolved in water and barium precipitated according to directions given under Procedure No. 1.

Amyl alcohol may be used in place of ether-alcohol by digesting the nitrates in a boiling solution (130° C.), calcium going into solution and barium and strontium remaining insoluble as nitrates.

Separation of the Alkaline Earths from Molybdenum.—The substance is fused with sodium carbonate and the fusion extracted with water and filtered. Molybdenum passes into the filtrate and the alkaline earths remain in the residue.

Separation of Phosphoric Acid from the Alkaline Earths.—Ammonium carbonate is added to the hydrochloric acid solution until a slight permanent turbidity is obtained, and the solution just cleared with a few drops of HCl. Ferric chloride is now added drop by drop until the solution above the yellowish white precipitate becomes brownish in color. The solution is diluted to about 400 ml. and brought to boiling and then filtered and the residue washed with water containing ammonium acetate. The filtrate contains the alkaline earths, free from phosphoric acid.

Separation from Lead.—If the ore has been treated with H_2SO_4, $BaSO_4$ and $PbSO_4$ will be found with SiO_2. In the acetate extraction of lead the presence of 1% ammonium sulfate eliminates the solubility of $BaSO_4$, but does not seriously interfere with the solubility of $PbSO_4$ in the ammonium acetate. $CaSO_4$ dissolves and accompanies lead. The investigation of Alldredge and Scott shows a complete extraction of $PbSO_4$ by means of ammonium acetate with no appreciable solution of $BaSO_4$. See chapter on Lead.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF BARIUM

For reasons given under "Preliminary Considerations," it is advisable to take a special sample for the determination of barium that has not undergone treatment with hydrogen sulfide or ammonium hydroxide, since these may cause the loss of barium as stated.

Barium in Insoluble Residue.—In the complete analysis of ores the residue remaining insoluble in acids is composed largely of silica, together with difficultly soluble substances, among which is barium sulfate. This residue is best fused in a platinum dish with sodium carbonate or a mixture of sodium and potassium carbonates (long fusion is not necessary). The cooled mass is digested with hot water to remove the soluble sodium compounds, silicate being included. Barium, together with the heavy metals, remains insoluble as carbonate and may be filtered off. The residue is now treated with dilute ammonia water to remove the adhering sulfates (testing the filtrate with hydrochloric acid and barium chloride solution; the washing being complete when no white precipitate of barium sulfate forms). The carbonates are washed off the filter into a 500-ml. beaker, the clinging carbonate being dissolved by pouring a few ml. of dilute, 1 : 1, hydrochloric acid on the paper placed in the funnel. This extract is added to the precipitate in the beaker and the latter covered to prevent loss by spattering. Additional hydrochloric acid is cautiously added so that the precipitate completely dissolves and the solution contains about 10 ml. of free hydrochloric acid (sp.gr. 1.2). Barium is precipitated from this solution best as a sulfate according to directions given later.

Silicates.—One gram of the finely pulverized sample is treated with 10 ml. of dilute sulfuric acid, 1 : 4, and 5 ml. of concentrated hydrofluoric acid. The mixture, evaporated to small bulk on the steam bath, is taken to SO_3 fumes on the hot plate. Additional sulfuric acid and hydrofluoric acid are used if required. By this treatment the silica is expelled and barium, together with other insoluble sulfates, will remain upon the filter when the residue is treated with water and filtered. Lead sulfate, if present, may be removed by washing the residue with a solution of ammonium acetate. Barium sulfate may be purified by fusion with potassium carbonate as above directed or by dissolving in hot concentrated sulfuric acid, and precipitating again as $BaSO_4$ by dilution.

Ores may be decomposed by either of the above methods or a combination of the two. Sulfide ores require roasting to oxidize the sulfide to sulfate.

Barium Sulfate is decomposed by fusion with sodium and potassium carbonates. The fusion is leached with water to remove the soluble sulfate and the residue, $BaCO_3$, is dissolved in HCl. Barium is determined in this solution.

DETERMINATION OF BARIUM AS A CHROMATE

A preliminary spectroscopic test has indicated whether a separation from calcium and strontium is necessary. If these are present, barium is separated along with strontium from calcium as the nitrate in presence of alcohol-ether mixture, according to directions given under "Separations." Barium is now precipitated as the chromate, $BaCrO_4$, from a neutral or slightly acetic acid solution, strontium remaining in solution.

Precipitation of Barium Chromate.—If barium is present in the form of nitrate, together with strontium, the mixed nitrates are evaporated to dryness and then taken up with water, about 10 ml. ammonium acetate (300 grams $NH_4C_2H_3O_2$ neutralized with $NH_4OH + H_2O$ to make up to 1000 ml.) added and the solution heated to boiling. Five ml. of 20% ammonium bichromate are added drop by drop with constant stirring and the precipitate allowed to

settle until cold. The solution is decanted off from the precipitate through a filter and washed by decantation with dilute (0.5%) solution of ammonium acetate until the excess chromate is removed, as indicated by the filtrate passing through uncolored. If much strontium was originally present, a double precipitation is necessary, otherwise the precipitate may be filtered directly into a Gooch crucible and dried (120° C.), to constant weight.

Purification from Strontium.—The precipitate is dissolved from the filter by running through dilute (1 : 5) warm nitric acid, poured upon the chromate, catching the solution in the beaker in which the precipitation was made; the least amount of acid necessary to accomplish this being used and the filter washed with a little warm water. Ammonium hydroxide is now added to the solution, cautiously, until a slight permanent precipitate forms and then 10 ml. of ammonium acetate solution added with constant stirring and the mixture heated to boiling. The precipitate is allowed to settle until the solution is cold and then filtered and washed by decantation as before, a Gooch crucible being used to catch the precipitate.

Ignition.—The precipitate is washed with dilute alcohol once, then dried at 110° C. The Gooch containing the $BaCrO_4$ is gently heated in a larger crucible (allowing an encircling air space around the Gooch) until the color of the chromate becomes uniform.

$$BaCrO_4 \times 0.6053 = BaO. \quad BaCrO_4 \times 0.5421 = Ba.$$

NOTES.—The use of sodium hydrate or acetate in place of the ammonium hydroxide and acetate is sometimes recommended, owing to the slight solubility of $BaCrO_4$ in ammonium salts, as seen by the following table, approximate figures being given:

100,000 parts of cold water dissolves	0.38 parts $BaCrO_4$
100,000 parts of hot water dissolves	4.35 parts $BaCrO_4$
100,000 of 0.5% solution of NH_4Cl dissolves	4.35 parts $BaCrO_4$
100,000 of 0.5% solution of NH_4NO_3 dissolves	2.22 parts $BaCrO_4$
100,000 of 0.75% solution of $NH_4C_2H_3O_2$ dissolves	2.00 parts $BaCrO_4$
100,000 of 1.5% solution of $NH_4C_2H_3O_2$ dissolves	4.12 parts $BaCrO_4$
100,000 of 1% acetic acid dissolves	20.73 parts $BaCrO_4$

Although the solvent action of ammonium salts is practically negligible under conditions of analysis given above, the solvent action of free acetic acid is of importance, so that it is necessary to neutralize or eliminate free mineral acids before addition of the acetate salt.

The edges of the $BaCrO_4$ precipitate upon drying may appear green, owing to the action of alcohol; upon ignition, however, the yellow chromate is obtained. The color orange yellow, when hot, fades to a light canary yellow upon cooling.

$BaCrO_4$, *mol.wt.*, 253.37; *sp.gr.*, $4.498^{15°}$; 100 ml. H_2O soln. cold will dissolve $0.00038^{18°}$ gram, hot dissolves 0.0043 gram; soluble in HCl, HNO_3, yellow rhombic plates.

Determination of Barium as Barium Carbonate.—The solution free from previous groups and from calcium and strontium is made ammoniacal; after addition of ammonium chloride if not already present for the purpose of preventing precipitation of magnesium. Ammonium carbonate is now added in slight excess and the precipitated $BaCO_3$ allowed to settle on the water bath or in a warm place for an hour or preferably longer. The precipitate is filtered and washed with dilute NH_4OH, dried and ignited and weighed as $BaCO_3$. The method proposed by Fresenius, is considered by some to be more accurate than the sulfate method.

$$BaCO_3 \times 0.696 = Ba.$$

DETERMINATION OF BARIUM BY PRECIPITATION AS SULFATE, $BaSO_4$

This method depends upon the insolubility of barium sulfate in water and in very dilute hydrochloric acid or sulfuric acid, one gram of the salt requiring about 344,000 ml. of hot water to effect solution.

Reaction, $BaCl_2+H_2SO_4=BaSO_4+2HCl$.

$BaSO_4$, *mol.wt.*, 233.42; *sp.gr.*, 4.47 *and* 4.33; *m.p.*, 1580° C. (*amorphous decomposes*); H_2O *dissolves* $0.00017^{20°}$ *and* $0.0003^{34°}$ *gram per* 100 *ml.* 3% HCl *dissolves* 0.0036 *gram. Soluble in conc.* H_2SO_4. *White, rhombic and amorphous forms.*

Procedure.—The slightly acid (hydrochloric) solution of barium chloride, prepared according to directions given, is heated to boiling (volume about 200–300 ml.) and a slight excess of hot dilute sulfuric acid added. The precipitate is settled on the water bath and the clear solution then decanted through a weighed Gooch crucible or through an ashless filter paper (S. and S. 590 quality). The precipitate is transferred to the Gooch (or paper), and washed twice with very dilute sulfuric acid solution (0.5% H_2SO_4), and finally with hot water until free of acid. The precipitate is dried and ignited, at first gently and then over a good flame to a cherry red heat, for half an hour. The residue is weighed as barium sulfate, $BaSO_4$.

$$BaSO_4\times0.5885=Ba, \text{ or } \times0.6570=BaO, \text{ or } \times0.8456=BaCO_3.$$

NOTES.—The determination of barium is the reciprocal of the determination of sulfur or sulfuric acid. Precautions and directions given for the sulfur precipitation apply here also, with the exception that dilute sulfuric acid is used as the precipitating reagent in place of barium chloride.

The author found that precipitation of barium sulfate in a large volume of cold solution containing 10 ml. of concentrated hydrochloric acid per 1600 ml. of solution, by adding a slight excess of cold dilute sulfuric acid in a fine stream, exactly in the manner that barium chloride solution is added in the precipitation of sulfur, and allowing the precipitate to settle, at room temperature, for several hours (preferably over night), gives a precipitate that is pure and does not pass through the Gooch asbestos mat. We refer to the chapter on Sulfur for directions for filtering, washing, and ignition of the residue.

The addition of hydrochloric acid causes rapid settling of the barium sulfate. F. A. Gooch has shown that the precipitation should be conducted at temperatures over 75° C., preferably at 90° C. "Methods in Chemical Analysis," 1912, page 168.

Lead, strontium and calcium should be absent. Cl, Al and Fe if present in appreciable amounts, will contaminate the $BaSO_4$.

VOLUMETRIC METHODS FOR THE DETERMINATION OF BARIUM

TITRATION OF THE BARIUM SALT WITH DICHROMATE

This method is of value for an approximation of the amount of barium present in a solution that may also contain calcium, strontium, and magnesium or the alkalies. It depends upon the reaction,

$$2BaCl_2+K_2Cr_2O_7+H_2O=2BaCrO_4+2KCl+2HCl.$$

N/10 $K_2Cr_2O_7$ (precipitation purposes) contains 7.355 grams pure salt per liter.

Procedure.—The solution containing the barium is treated with ammonia until it just smells of it. (If an excess of ammonia is present the solution is made faintly acid with acetic acid.) It is then heated to about 70° C. and the standard dichromate added, with stirring until all the barium is precipitated and the clear supernatant solution is a faint yellow color from the slight excess of the reagent. For accurate work it is advisable to titrate the precipitate formed by one of the methods given below. One ml. $K_2Cr_2O_7=0.00687$ gram Ba. (Note reaction given above.)

NOTE.—*An excess of potassium dichromate may be added, the precipitate filtered off, washed and the excess of dichromate determined as stated below.*

REDUCTION OF THE CHROMATE WITH FERROUS SALT AND TITRATION WITH PERMANGANATE

Ferrous sulfate reacts with barium chromate as follows:

$$2BaCrO_4+6FeSO_4+8H_2SO_4=3Fe_2(SO_4)_3+Cr_2(SO_4)_3+2BaSO_4+8H_2O.$$

An excess of ferrous salt solution is added and the excess determined by titration with N/10 $KMnO_4$ solution. $Fe=\frac{1}{3}Ba$.

Reagents.—N/10 solution of $KMnO_4$. N/10 $FeSO_4\cdot7H_2O$ (27.80 grams per liter) or $FeSO_4\cdot(NH_4)_2SO_4\cdot6H_2O$ (39.213 grams per liter). One ml. $=0.004579$ Ba.

Procedure.—The well-washed precipitate of barium chromate is dissolved in an excess of standard N/10 ferrous ammonium sulfate solution containing free sulfuric acid. The excess ferrous salt is titrated with standard N/10 potassium permanganate solution.

(Ml. N/10 ferrous solution minus ml. permanganate titration) multiplied by 0.004579 gives grams barium in the solution. Iron factor to barium is 0.8200.

POTASSIUM IODIDE METHOD

The procedure depends upon the reactions:

1. $2BaCrO_4+6KI+16HCl=2BaCl_2+2CrCl_3+6KCl+8H_2O+6I.$
2. $3I_2+6Na_2S_2O_3=6NaI+3Na_2S_4O_6$

Procedure.—The precipitate, $BaCrO_4$, is dissolved in 50 to 100 ml. of dilute hydrochloric acid and about 2 grams of solid potassium iodide salt added and allowed to react about ten minutes. The liberated iodine is now titrated with N/10 thiosulfate. Near the end of the titration starch solution is added and followed by N/10 thiosulfate until the color disappears.

One ml. N/10 $Na_2S_2O_3$ = 0.004579 gram Ba.

TITRATION OF BARIUM CARBONATE WITH STANDARD ACID

To the well-washed barium carbonate, $BaCO_3$, an excess of N/10 H_2SO_4 is added and the excess acid determined.

One ml. N/10 acid = 0.00687 gram Ba.

TITRATION OF THE BARIUM SALT WITH STANDARD SULFATE SOLUTION

Sodium rhodizinate has been proposed as an indicator for this titration.[8] Tetrahydroxyquinone is a more satisfactory indicator and may be added to the solution to be titrated.[9] The barium solution should be below 0.05 N with respect to hydrochloric acid and should be at room temperature. To each 50 ml. of solution should be added 15 ml. of alcohol. Chloride, carbonate, silicate, calcium, magnesium and aluminum do not interfere unless they are present in high concentration.

Indicator.—One part of the disodium salt of tetrahydroxyquinone is ground with 400 parts of dried potassium chloride, and 0.2 g. of this mixture is used, measured by a small cup. The solution of the indicator is unstable.

The solution is titrated with standard potassium sulfate, 0.05 M, to the disappearance of the red color of the barium salt of the indicator.

ANALYSIS OF BARITE AND WITHERITE

Barite or heavy spar is a variety of native barium sulfate, and witherite a native barium carbonate. These minerals are typical examples of barium-bearing ores. The analysis may involve the determination of barium and calcium sulfates or carbonates, magnesia, iron and aluminum oxides and

[8] Giblin, Analyst, **58**, 752 (1933); Friedrich and Rapoport, Mikrochemie, **14**, 41 (1933). The solution is spotted on paper.

[9] Schroeder, Ind. Eng. Chem., Anal. Ed. **5**, 403 (1933). The reverse titration is described in the Chapter on Sulfur.

moisture. Traces of lead, copper, and zinc may be present, as well as sulfide, sulfur and fluorine in fluorspar.

PROCEDURE FOR COMMERCIAL VALUATION OF THE ORE[10]

Solutions Required (For Barium and Strontium)

1. **Ammonium Acetate.**—Dissolve 300 g. $NH_4C_2H_3O_2$ in distilled water and dilute to 1000 ml.

2. **Ammonium Acetate, Dilute.**—20 ml. of solution 1 are diluted to 1000 ml.

3. **Ammonium Dichromate.**—Dissolve 100 g. $(NH_4)_2Cr_2O_7$ (free from SO_3) in distilled water and dilute to 1000 ml.

4. **Ammonium Hydroxide** (1 : 5).—Mix 200 ml. of NH_4OH (sp.gr. 0.90) with 1000 ml. of distilled water.

5. **Ammonium Sulfate.**—Dissolve 30 g. $(NH_4)_2SO_4$ (C.P.) in distilled water and dilute to 1000 ml.

6. **Ammonium Sulfate, Dilute.**—Dissolve 2 g. of $(NH_4)_2SO_4$ (C.P.) in distilled water and dilute to 1000 ml.

7. **Hydrochloric Acid** (1 : 4).—Mix 200 ml. of HCl (sp.gr. 1.20) with 800 ml. of distilled water.

8. **Nitric Acid** (1 : 4).—Mix 200 ml. of HNO_3 (sp.gr. 1.42) with 800 ml. of distilled water.

9. **Sodium Carbonate.**—Dissolve 2 g. Na_2CO_3 (C.P.) in distilled water and dilute to 1000 ml.

10. **Sulfuric Acid** (1 : 1).—Mix cautiously 500 ml. of H_2SO_4 (sp.gr. 1.84) with 500 ml. of distilled water.

11. **Ethyl Alcohol Solution.**—Mix 100 ml. of ethyl alcohol (95%) with 100 ml. distilled water and add 1 ml. of H_2SO_4 1 : 1.

Barium Sulfate

1. **Method for Barite Essentially Free from Strontium.**—Weigh 1 g. of sample into a platinum crucible and add 8 g. of sodium carbonate (C.P.) (1).[11] Cover and fuse the mixture over a Meker burner for 40 minutes (2). Cool (3) and leach out the fusion with 200 ml. of hot water in a 400-ml. beaker. Filter (4), washing the paper and residue 12 times with the hot sodium carbonate solution. (Reserve this filtrate for the determination of SO_3.)

Dissolve (5) the carbonates from the paper and crucible with hot HCl(1 : 4), catching the solution in a 600-ml. beaker, and wash the paper with hot water until free of chlorides.

Neutralize (6) this solution with NH_4OH (sp.gr. 0.90) and add 0.4–0.6 ml. of HCl (sp.gr. 1.20). Dilute to 400 ml. with hot distilled water, bring the solution to boiling, and add 25 ml. (±0.5 ml.) of hot ammonium sulfate solution (solution No.5) dropwise with constant stirring (7). Transfer the beaker to a warm plate and allow to stand for at least four hours. Filter on an ignited weighed Gooch crucible (8), wash (9) thoroughly with hot water and ignite the crucible in a muffle for 35 minutes at 850° C. Cool in a desiccator and weigh.

[10] Standard Method of the New Jersey Zinc Company.
[11] Notes. See pp. 132 and 133.

Make a blank determination in a similar manner on an equal amount of sodium carbonate and other reagents reserving the first filtrate for blank determination of SO_3.

Calculate the per cent of $BaSO_4$ as follows:

$$(A - B - C) \times 100 = \%\ BaSO_4,$$

where A is the weight in grams of the Gooch crucible and the barium sulfate,
B is the weight in grams of the ignited Gooch crucible,
C is the weight in grams of the blank determination.

2. Method for Barite Containing an Appreciable Percentage of Strontium.—Weigh 1 g. of sample into a platinum crucible and add 8 g. of sodium carbonate (C.P.) (1). Cover and fuse the mixture over a Meker burner for 40 minutes (2). Cool (3) and leach out the fusion with 200 ml. of hot water in a 400-ml. beaker. Filter (4), washing the paper and residue 12 times with hot sodium carbonate solution. (Reserve the filtrate for the determination of SO_3.)

Dissolve (5) the carbonates from the paper and crucible with hot HNO_3 (1 : 4), catching the solution in a 600-ml. beaker, and wash the paper well with hot water. Cool, neutralize with NH_4OH (sp.gr. 0.90) and make the solution just acid with HNO_3 (1 : 4). Dilute to 300 ml. with water and add 10 ml. of ammonium acetate solution. Heat to boiling and add while stirring 20 ml. of ammonium dichromate (10) solution. Let stand on a warm plate for 3 hours or more, filter the supernatant liquid (11) and wash by decantation with dilute ammonium acetate solution (12). Discard the filtrate.

Dissolve the precipitate on the paper with warm HNO_3 (1 : 4) into a 600-ml. beaker and wash with hot water. Dilute to 300 ml. and add ammonium hydroxide solution (1 : 5) slowly with stirring until the precipitate forming again no longer dissolves. Add 10 ml. ammonium acetate solution and 5 ml. ammonium dichromate solution, and bring the liquid to boiling while swirling; let stand on a warm plate 2 hours or more, filter (11) and wash once with dilute ammonium acetate solution. Discard the filtrate.

Dissolve the precipitate into a 600-ml. beaker with hot HCl (1 : 4) and wash paper with hot water until free from chlorides.

Add 10 ml. H_2O_2 (3%) and 25 ml. ethyl alcohol (95%), boil for 5 minutes (13), cool, neutralize (14) with NH_4OH (sp.gr. 0.90) and add 0.4–0.6 ml. of HCl (sp.gr. 1.20). Dilute to 400 ml. with hot distilled water, heat to boiling, and add 40 ml. of hot ammonium sulfate solution dropwise with stirring. Let stand on a warm plate for four hours or more. Filter on an ignited weighed Gooch crucible (8), wash (9) thoroughly with hot dilute $(NH_4)_2SO_4$ solution, and ignite the crucible in a muffle furnace for 35 minutes at 850° C. Cool and weigh. Make a blank determination on an equal amount of sodium carbonate and other reagents reserving the first filtrate for blank determination of SO_3.

Calculate the per cent of $BaSO_4$ as described at the end of method 1 above. (Numbered notes are at the end of the next section.)

Strontium Sulfate

Gravimetric Determination in Barite Concentrates.—Weigh 2 g. of sample into a platinum crucible and add 10 g. of sodium carbonate (C.P.) (1). Cover

and fuse the mixture over a Meker burner for 1 hour (2). Cool (3) and leach out the fusion with 200 ml. of hot water in a 400-ml. beaker. Filter (4), washing the paper and residue 12 times with hot sodium carbonate solution.

Dissolve (5) the carbonates from the paper and crucible with hot HNO_3 acid (1 : 4), catching the solution in a 400-ml. beaker, and wash the paper well with hot water. Evaporate to about 50 ml. and transfer to a 150-ml. beaker. Continue evaporation to dryness at 125–135° C. (15).

Disintegrate the dried residue as thoroughly as possible with a glass rod, add 25 ml. of hot absolute amyl alcohol and leach thoroughly by agitation with the rod (16). Let stand on a warm plate 3 or more hours, filter (17) and wash twice with 5 ml. portions of hot absolute amyl alcohol.

Dissolve the nitrates from the paper and from the 150-ml. beaker with hot water into a 600-ml. beaker, dilute to 300 ml. with water and add 10 ml. ammonium acetate solution. Heat to boiling and add while stirring 30 ml. ammonium dichromate (10) solution. Let stand on a warm plate for 3 hours or more, filter the supernatant liquid (11) into a 1000-ml. beaker and wash by decantation with dilute ammonium acetate solution (12). Dissolve the precipitate on the paper with warm HNO_3 (1 : 4) into the 600-ml. beaker and wash with hot water. Dilute to 300 ml. and add ammonium hydroxide solution (1 : 5) slowly with stirring until the precipitate forming again no longer dissolves. Add 10 ml. ammonium acetate solution and 5 ml. ammonium dichromate solution, bring the liquid to boiling while swirling, let stand on a warm plate for 2 hours or more, filter (11) into the 1000-ml. beaker and wash once with dilute ammonium acetate solution.

Make the solution in the 1000-ml. beaker slightly acid with HNO_3 (sp.gr. 1.42) and evaporate to about 100 ml. volume (18). Transfer to a 250-ml. beaker, add 10 ml. NH_4OH (sp.gr. 0.90) and 3 g. powdered $(NH_4)_2CO_3$ (C.P.) and heat to boiling (19). Let stand on a warm plate for 2 hours or more, filter (20) and wash once with hot water.

Dissolve the precipitate into the original beaker with HCl (1 : 4) and evaporate to about 10 ml. volume. Add 50 ml. H_2SO_4 (1 : 1) and 60 ml. ethyl alcohol (95%). Stir, allow to stand for 12 hours or more, filter and wash well with ethyl alcohol solution (1 : 1) and finally with ethyl alcohol (95%). Dry the paper and precipitate in a weighed platinum crucible, char paper at a low temperature and ignite at dull redness, cool and weigh. Make a blank determination in similar manner on an equal amount of sodium carbonate and other reagents.

Calculate the per cent of $SrSO_4$ as follows:

$$\frac{A - B - C) \times 100}{2} = \%\ SrSO_4,$$

where A is the weight in grams of the crucible and strontium sulfate,
B is the weight in grams of the platinum crucible initially,
C is the weight in grams of the blank determination.

Notes on the Determination of Barium Sulfate and Strontium Sulfate. (Numbers correspond to those in the procedures.)

1. The crucible is prepared as follows: A layer of sodium carbonate about ¼″ deep is placed in the bottom of the crucible, the sample placed on top of this, and both mixed with a glass rod. The rest of the Na_2CO_3 is then added to the crucible.

2. The fusion is started with a low flame which is gradually raised to full blast. This precaution is necessary to prevent loss by overflowing.

3. As the melt cools, rotate the crucible so that the fusion will solidify in a thin layer. This will shorten the time required for leaching.

4. Use a No. 40 Whatman 15 cm. filter or similar paper. Wash several times by decantation, then remove the crucible from the beaker, transfer the insoluble carbonates to the filter, and wash with hot sodium carbonate solution, testing after the twelfth washing to be certain that sulfates have been removed completely.

5. Cover the funnel containing the carbonates with a watch glass and add the acid, carefully, in small portions at a time to prevent loss. Add hot dilute acid to the platinum crucible and cover in the beaker in which the leach was made and pour over the filter.

6. Use methyl orange as the indicator.

7. This procedure is necessary to prevent coprecipitation of calcium and strontium.

8. The Gooch crucible should be of platinum and ignited with asbestos pad to constant weight.

9. Wash with hot water several times by decantation. The beaker should be scrubbed thoroughly to remove any adhering barium sulfate Continue the washing until free of chlorides.

s precipitated as $BaCrO_4$.

11. Use a No. 40 Whatman 15 cm. filter or similar paper.

12. Use several portions of dilute ammonium acetate solution totaling about 100 ml.

13. To reduce the chromium completely.

14. The precipitation of $Cr(OH)_3$ serves as an indicator. The solution should be made slightly acid with HCl (sp.gr. 1.20) before adding the excess.

15. The sample should be held at 125–135° C. until thoroughly dry and ready to proceed.

16. Calcium nitrate is dissolved. Boil the absolute amyl alcohol for a few minutes before using. Equal volumes of ethyl alcohol and absolute ether may be used in place of the absolute amyl alcohol. One extraction is sufficient for samples containing less than 3% CaO.

17. Use a No. 40 Whatman 9 cm. filter or similar paper.

18. The concentration should be carried no further to prevent reduction of the chromates.

19. The strontium is precipitated as $SrCO_3$.

20. Use a No. 40 Whatman 9 cm. filter or similar paper.

Total Sulfur as SO_3

The filtrate containing the SO_3 and the washings from the barium carbonate is oxidized by warming with 10 ml. of H_2O_2(3%), neutralized with HCl (sp.gr. 1.20) and 1–1.5 ml. added in excess, concentrated to proper volume, and the sulfate is precipitated from the boiling solution by adding hot 10% $BaCl_2$ solution. The filtration, washing and final ignition are made in the usual fashion. The blank is determined in the same manner.

Silica

One gram of the sample is weighed into a platinum crucible and fused with sodium carbonate as under Barium Sulfate. The fusion is leached out in a 150 ml. platinum dish with hot water. Leaching is carried on until disintegration of the fusion is complete. The residue, composed of mixed carbonates, silicates, etc., is filtered off, catching filtrate in a 400-ml. beaker, and washed thoroughly with hot water containing sodium carbonate. The residue on the paper and in the crucible is dissolved with hot dilute hydrochloric acid, catching in a separate 400-ml. beaker, and the paper thoroughly washed with hot water. This paper containing a portion of the silica is placed in a platinum crucible and retained.

The first filtrate, from the barium carbonate, is acidified with HCl and evaporated to dryness to dehydrate the silica. The second solution, containing the barium in solution as chloride is also evaporated to dryness. After dehydrating, the residues in both beakers are taken up with dilute HCl and filtered. They may be filtered through the same paper, washing the paper thoroughly before passing the second solution. The first filtrate, from the barium carbonate, is again evaporated to dryness, taken up and filtered as before on a new paper. After the papers are thoroughly washed with hot water, they are added to the original paper in the crucible, ignited and weighed. The contents of the crucible are treated with hydrofluoric and sulfuric acids, evaporated to dryness, ignited and weighed. The difference in weight is amount of silica present.

Iron

Two grams of the sample are weighed into a 250 ml. beaker, moistened with water, 15 ml. concentrated hydrochloric acid and 10 ml. concentrated nitric acid added. After digesting a short time 10 ml. dilute sulplurie acid (1 : 1) are added and the solution evaporated to complete dryness. 10 ml. concentrated hydrochloric acid and 25 ml. water are added and heated to boiling. The iron is reduced with stannous chloride solution. The reduced solution and residue are washed into a 600 ml. beaker containing 15 ml. titrating solution and diluted to 400 ml. with cold water. After standing for 3 minutes, the iron is titrated with standard potassium permanganate solution. The titrating solution is prepared and the reduction and titration are conducted according to the details given in the chapter on Iron.

Iron and Alumina

The two filtrates from the silica determination are reduced in volume and nearly neutralized with ammonium hydroxide (acidity 1 ml. hydrochloric acid), and combined. Ammonium sulfate solution is added to assure complete precipitation of all the barium, the beaker placed on a steam plate for two hours. The barium sulfate is then filtered off. The iron and alumina in the filtrate are precipitated with ammonium hydroxide, the precipitate filtered off, dissolved with dilute hydrochloric acid, reprecipitated and filtered, washed with 2% ammonium nitrate solution, ignited in a platinum crucible and weighed.

Lime

The filtrate from the precipitated iron and alumina is acidified slightly with hydrochloric acid, boiled down to a volume of less than 100 ml. and filtered if necessary. The solution is now made ammoniacal, heated to boiling, and 10 ml. of ammonium oxalate solution added. After standing for two hours in a warm place the precipitate of calcium oxalate is filtered off, washed with hot water, ignited and weighed as calcium oxide.

Magnesia

The filtrate from the lime determination is acidified with hydrochloric acid, evaporated to about 200 ml., cooled to room temperature and 15 ml. micro-

cosmic salt (saturated solution) added. Ammonium hydroxide is added with 40 ml. in excess and the precipitate allowed to settle over night. The precipitate is then filtered off, dissolved with hydrochloric acid (1 part concentrated acid to four parts of water), diluted to 100 ml., 10 ml. of microcosmic salt solution added, followed by ammonium hydroxide with 40 ml. excess and allowed to stand over night. The precipitate of magnesium ammonium phosphate is filtered off, washed, carefully ignited and weighed.

Carbon Dioxide

The carbon dioxide is determined according to method given for carbonates under chapter on Carbon. It is necessary to use a large sample, i.e., 5–10 grams, and for samples containing a small amount of carbonates a Geissler absorption bulb is preferable to the heavy Fleming type bulb.

Fluorine

One gram of sample is placed in a lead bomb with 12 ml. of sulfuric acid (sp.gr. 1.84), the bomb closed with glass plate in place and heated in an oil bath

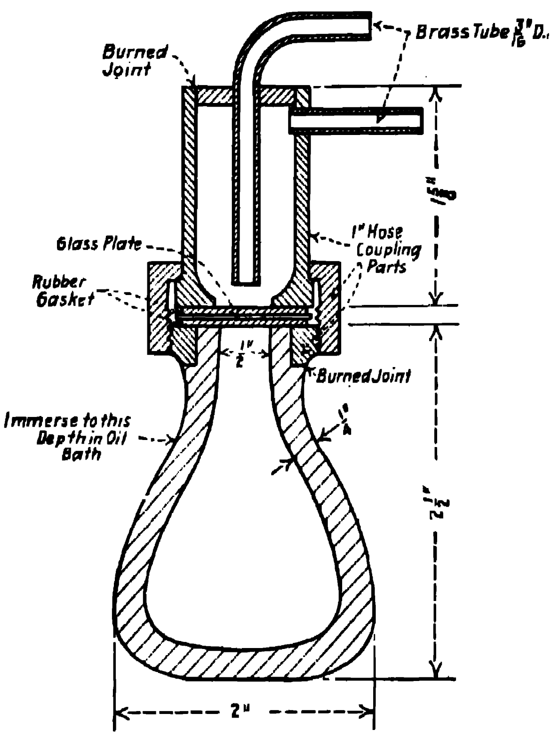


Fig. 15.—Apparatus for Fluorine Determination.

for 45 minutes at 165° C. The etching on the glass plate is compared with etching using known amounts of fluorine as CaF_2 and the same kind of glass.

The glass plate is kept cool by circulating cold water. The type of bomb and its connections are shown in Fig. 15.

Loss on Ignition

One gram of the sample is weighed out into a platinum crucible, dried at 110° C. for two hours and weighed. This moisture is to be used for calculating all results to a dry basis. The crucible is heated gently at first and then placed in a muffle furnace or over a blast lamp and ignited until it ceases to lose weight on reheating. This loss is calculated to a basis of one gram of dry material.

BLANC FIXE

The sulfate of barium is generally marketed as paste and less commonly in the dry form. Both pulp and dry forms should contain not less than 97.5 per cent $BaSO_4$ on the dry basis. The pulp (paste) should not contain over 30 per cent H_2O. Blanc Fixe is used in photography, in coating paper and in paint.

Qualitative Tests. Suitability for photographic purposes.—Spread a sample on a glass plate and apply a drop of 10 per cent $AgNO_3$ solution. Set aside in a dark closet. No dark brown or black stain should be evident in five minutes.

Alumina and Iron.—Heat a small portion with HNO_3, dilute and filter. Test the filtrate with NH_4OH. A gelatinous colorless precipitate $= Al(OH)_3$, a red precipitate $= Fe(OH)_3$ and possibly $Al(OH)_3$ with the iron.

Lead.—Extract a small portion with ammonium acetate and test the extract with $K_2Cr_2O_7$. A yellow precipitate indicates $PbCrO_4$, showing the presence of $PbSO_4$.

Silica.—Test about 0.5 g. with 10 ml. conc. H_2SO_4, complete solution shows the absence of SiO_2.

Organic Matter.—Coloration of the acid in the silica test indicates the presence of organic matter.

Carbonates.—Addition of acid will cause effervescence in presence of carbonate.

Phosphates.—Extract a small portion with HNO_3 and test the extract with ammonium molybdate for phosphate.

Quantitative Analysis.—The qualitative tests will indicate the presence of impurities. These can now be determined by the standard procedures. The following brief outline may be found useful as a guide for the method of examination.

Moisture.—Determine loss on 2-gram sample dried at 105° C. for two hours.

Loss on Ignition.—Ignite residue from above. Loss is due to escape of CO_2 and to organic matter and combined water.

Iron and Alumina.—Digest a 5-gram sample with 150 ml. HCl (1 : 3). Evaporate extract to dryness, take up with 100 ml. dilute HCl and filter to remove SiO_2. Precipitate iron and alumina in filtrate in usual manner and determine. If P_2O_5 is present it will be present with the precipitate. If present it will be necessary to add a known quantity of iron as $FeCl_3$ to carry down all the P_2O_5. This iron and the P_2O_5, determined on a separate sample, must be deducted, to obtain the iron and alumina in the sample.

Phosphate.—Extract a 2-gram sample with water by decantation. Digest the residue with a 10% solution of HNO_3 and filter. Precipitate P_2O_5 in the filtrate with ammonium molybdate in the usual manner. The yellow precipitate is dissolved in NH_4OH and P_2O_5 precipitated with magnesia mixture and determined by the standard procedure.

$$Mg_2P_2O_7 \times 0.6379 = P_2O_5 \qquad Mg_2P_2O_7 \times 2.7040 = Ba_3(PO_4)_2$$

Lead Sulfate.—This may be determined in the residue from the iron and alumina determination by extraction with ammonium acetate and precipitation with dichromate reagent by usual procedure. $PbCrO_4 \times 0.9383 = PbSO_4$.

For Other Ingredients consult chapter on Paint Analysis.

BERYLLIUM [1]

Be, *at.wt.* 9.02; *sp.gr.* $1.85^{20°}$; *m.p.* > 1350° C.; *oxide*, BeO

Beryl is the chief source of beryllium; large crystals weighing as much as 2900 pounds, 12–14 feet long and 2–3 feet in diameter have been found. Emeralds are beryl crystals, colored green by traces of chromium. Beryllium occurs in granites, quartzose, gneiss, beryllonite, sodic rocks, euclase, danalite, chrysoberyl, helvite, leucophanite, hambergite. It is frequently associated with yttrium, zirconium, cerium in the minerals gadolinite and crytolite.

DETECTION

The solution from which silica has been removed, is treated in presence of free acid with H_2S to remove the members of this group. The sulfides are filtered off and the filtrate boiled to expel H_2S, and the iron oxidized by the addition of HNO_3 or H_2O_2. A large excess of NaOH is added and the iron (Ti, Zr, etc.) filtered off. Beryllium (accompanied by Al) passes into the filtrate. The alkaline filtrate is acidified by addition of HNO_3, and then made slightly alkaline with NH_4OH. Beryllium (and aluminum) precipitate. The precipitate is dissolved in a slight excess of acid, the solution is made almost

[1] Vauquelin (1798) was the first to separate beryllium from aluminum by the action of KOH. The metal was obtained by Bussy and Wöhler by reducing the chloride with potassium. The element was first named glucinum.

The difficulty in the metallurgy of beryllium has limited its extended use as a metal ($200 per pound in 1930). It forms a valuable alloy with aluminum for lighter than air craft on account of its conferring hardness, resistance to corrosion, increased tensile strength and low coefficient of expansion to the alloy. It has been found to be useful as a catalyst in combination with aluminum and cobalt for oxidation of ammonia to nitric acid.

The mineral beryl contains approximately 14 per cent of beryllium oxide, BeO, and is the principal source of beryllium. Beryllium is used in alloys. The aluminum alloy has considerable tensile strength, is hard and light (sp.gr. 2.5 with 90% Al and 10% Be). Beryllium added to alloys of copper and aluminum makes a tougher and more malleable product. (85% Al, 10% Be, 5% Cu, sp.gr. 2.8 with tensile strength equal to that of bronze.) Alloys of beryllium and copper are valuable for making scientific instruments on account of their electrical properties. Beryllium oxide is used in incandescent mantles. It acts as an accelerator for catalyzers. Ind. Eng. Chem., **16**, 74 (1924).

neutral by addition, dropwise, of dilute NH_4OH and solid sodium bicarbonate added in sufficient amount to make the solution contain 10% of the reagent. The mixture is heated gently, but not boiled, and then filtered. $Al(OH)_3$ remains on the filter and beryllium goes into the filtrate. The filtrate is diluted with ten volumes of water and boiled. Beryllium hydroxide precipitates.

If PO_4^{---} is present it is removed by precipitation in acid solution by addition of ammonium molybdate and filtered off. The beryllium is determined in the filtrate, the ammonium molybdate causing no interference.

Beryllium may be confirmed by adding a few drops of quinalizarin (5% reagent in 0.25 N NaOH) to 10 ml. of the solution (freed from Al by directions above) and making alkaline with 0.25 N NaOH. A blue color results. This should be compared with a blank test of the reagent added to 0.25 N NaOH, which gives a violet color. (See directions following.)

Beryllium hydroxide is insoluble in excess of NH_4OH, distinction from aluminum. It is soluble in an excess of fixed alkalies, distinction from iron. It dissolves in an excess of ammonium carbonate, distinction from aluminum.

Test for Beryllium.—The following test is recommended by H. Fisher (Wissenschaftliche Veroffentlichungen aus dem Siemens-Konzern, **2**, 99, 1926). The precipitate, as obtained above, is dissolved in acid, and carefully neutralized with pure NaOH (free from Mg). Ten ml. of the neutralized solution is treated with 5 ml. of 2N NaOH and then with 2 to 3 drops of 0.05 per cent solution of quinalizarin dye (1, 2, 5, 8-Tetrahydroxyanthraquinone, alizarin bordeaux) in 0.25 N NaOH. (If preferred 10–15 drops of a 0.01% solution of the dye in absolute alcohol may be used.) The test is conducted, if desired, in Nessler tubes. A blank run is made with water and the reagents used. Beryllium colors the solution blue (compare against a white background). The blank will be colored violet-red. Aluminum does not interfere. Phosphates, tartrates, iron and magnesium must not be present.

ESTIMATION

In analytical processes the element accompanies aluminum in the general procedure of separations and if not detected it will be reported as aluminum.

The methods of preparation and solution of the sample are given under the chapter on aluminum. The following solubilities are of interest:—The freshly precipitated hydroxide of beryllium is easily soluble in dilute acids, in alkalies, in alkali carbonates and bicarbonates. The oxide dissolves in concentrated sulfuric acid. It is decomposed by fusion with potassium fluoride.

In estimations of beryllium the material is best decomposed with Na_2CO_3 fusion, followed by treatment with HCl, evaporation to dryness, taking up with

HCl and water and filtering from silica according to the general procedure. The filtrate contains beryllium, if present in the ore.

SEPARATIONS

Separation from Silica.—See introductory paragraph.

Separation from Hydrogen Sulfide Group.—See Detection.

Separation from Iron, Titanium, Zirconium, the Rare Earths and Chromium.—The hot, slightly acid solution is poured into an excess of sodium hydroxide solution (after oxidation with HNO_3) and boiled. Beryllium, aluminum, germanium, vanadium, phosphorus pass into the filtrate.

Separation from Aluminum (Phosphates absent).—The solution from iron is nearly neutralized with HCl and the clear solution poured into a warm solution of sodium bicarbonate. Additional solid sodium bicarbonate is added to make the solution contain approximately 10% $NaHCO_3$. Heat just to boiling and filter. Cool and filter. Wash the precipitate with small portions of hot water. The filtrate contains the beryllium. The precipitate of aluminum should be dissolved and the precipitation repeated to recover any occluded beryllium. This is precipitated as stated above (the two filtrates being combined).

In presence of phosphates the phosphate is precipitated with ammonium molybdate as stated under Detection and aluminum and beryllium precipitated as hydroxides and separated as stated above.

Separation from Aluminum by the 8-Hydroxyquinoline Method.[2]—The solution very faintly acid (1–2 drops HCl per 100 ml.) is gently warmed to about 55–60° C. and about 40–50% excess of acetic acid solution of 8-hydroxyquinoline reagent [3] is added to the warmed solution, and then very slowly a 2 N ammonium-acetate solution, until a permanent precipitate is obtained. Settle, filter and wash. Aluminum is precipitated and beryllium passes into the filtrate.

Separation from Aluminum by the Hydrochloric Acid Method.—Consult the chapter on aluminum.

GRAVIMETRIC DETERMINATION OF BERYLLIUM

The most common way of determining beryllium is by precipitation with ammonium hydroxide and ignition to beryllium oxide. Because of the colloidal nature of the precipitate the results are likely to be high. The following methods of precipitating beryllium hydroxide appear to be more advantageous.

[2] The reagent precipitates Al, Fe and Cu but not Be (Z. Anal. Chem., 76, 135, 1929.)

[3] 8-hydroxyquinoline reagent is prepared by dissolving 5 grams of the powdered compound in 100 ml. of 2N acetic acid. One ml. will precipitate 0.0027 g. Al.

Procedure.—To the slightly acid solution containing about 0.1 gram of beryllium oxide in 100 ml., add sodium carbonate until a slight permanent turbidity results. Dissolve this in hydrochloric acid, heat to 70° C., and while passing a current of air through the solution, add 50 ml. of 6% ammonium nitrite, and then, while stirring, add 20 ml. of methyl alcohol. The current of air helps to expel NO and NO_2 and the methyl alcohol serves to remove nitrous acid as nitrous ester. If only a little Na_2CO_3 is used in the neutralization, this precipitate may be fully washed with a 2% solution of ammonium acetate containing free ammonia, and ignited directly to BeO.

If much Na_2CO_3 is used it will be necessary to redissolve and reprecipitate in the same way.

The procedure recommended by Parsons and Barnes [4] depends upon the solubility of beryllium hydroxide in a 10% sodium bicarbonate solution, in the separation of this element from iron and aluminum hydroxide precipitate, with which it is commonly thrown out from solution. (Uranium, if present, also dissolves.)

Procedure.—Silica and the members of the hydrogen sulfide group having been removed by the usual methods (See Detection), hydrogen sulfide is expelled by boiling, nitric acid is added in sufficient amount to oxidize iron (the hydrochloric acid solution turns yellow) and ammonium hydroxide added in slight excess. The precipitated hydroxides are allowed to coagulate by heating to boiling and, after settling a few minutes, filtered and washed with a 2% solution of ammonium acetate containing free ammonia.

Separation from Iron and Aluminum Hydroxide.—The precipitate is dissolved in hydrochloric acid, the solution oxidized with nitric acid or hydrogen peroxide (C.P.), if necessary, and the free acid then neutralized with ammonia. To the cold solution are added 10 grams of sodium bicarbonate for each 100 ml. of liquid. The mixture is heated to boiling and boiled for one minute,[5] then cooled and filtered. The residue is washed with hot 10% solution of sodium bicarbonate. Iron and aluminum hydroxides remain on the filter and beryllium passes into the filtrate.

To recover occluded beryllium from the hydroxides of iron and alumina, the precipitate is dissolved in a few drops of hydrochloric acid, and the precipitation repeated. It is advisable to repeat this treatment a third time, adding the filtrates to the first portion containing the beryllium.

Precipitation of Beryllium.—The combined filtrates from the alumina and iron hydroxides are acidified with strong hydrochloric acid, the beakers covered to prevent loss by spurting and the carbon dioxide completely removed by boiling. (CO_2 remaining in solution would form ammonium carbonate, on subsequent treatment with ammonia, which would dissolve beryllium.) A slight excess of ammonia is now added, the mixture again boiled and the precipitated beryllium hydroxide allowed to settle, then filtered and washed several times with a 2% solution of ammonium acetate containing free ammonia. To free beryllium hydroxide from occluded sodium salts, the precipitate is redissolved in as little HCl as possible, the solution diluted to 100 ml. and the precipitation with ammonium hydroxide is repeated, finally washing with a 2% solution of

[4] C. L. Parsons and S. K. Barnes, J. Am. Chem. Soc., 28, 1589, 1906.

[5] Prolonged boiling would cause the loss of too much CO_2, so that $Al(OH)_3$ would be apt to pass into solution. The evolution of CO_2 may be mistaken for boiling.

ammonium acetate containing free ammonia until the chlorides are removed. After ignition the residue is weighed as beryllium oxide, BeO.

$$BeO \times 0.3605 = Be.$$

PHOSPHATE METHOD

To the slightly acid solution of sulfate or nitrate contained in an Erlenmeyer flask, add 5 grams of secondary acid ammonium phosphate, 20 grams of ammonium nitrate, and 30 ml. of a cold saturated solution of ammonium acetate. Heat to boiling and dissolve the precipitate by adding as little 6N nitric acid as possible from a pipette. Then, slowly add from a burette at the rate of 5–6 drops a minute, 1.5N ammonium hydroxide until a good precipitation results of crystalline beryllium ammonium phosphate. Make the solution distinctly ammoniacal, allow to cool, and make ammoniacal to phenolphthalein. After the precipitation has settled, or preferably after it has stood overnight when little beryllium is present, filter, wash till free from phosphate with a hot, 5% solution of ammonium nitrate, ignite and weigh.

8-HYDROXYQUINOLINE METHOD[5]

Procedure.—Use a 5 gram sample if the beryllium content is less than 0.25%, and 1 or 0.5 grams if higher percentages are expected.

Dissolve the sample in hydrochloric acid using 20 ml. per gram of sample. Saturate the solution with hydrogen sulfide. Filter off the precipitated sulfides and any undissolved material present, and wash free from acid. Boil off the hydrogen sulfide, and evaporate until the solution begins to crystallize, wash down the sides of the beaker, cool, add an equal volume of ether, and pass dry hydrogen chloride through the solution until the two phases are completely miscible and for an hour afterward. To avoid excessive loss of ether, it is well to cool the beaker during the saturation with hydrogen chloride. Filter through the Gooch crucible or similar device, refiltering if the filtrate is cloudy. Wash thoroughly with a solution made by saturating with hydrogen chloride a 1 : 1 mixture of ether and hydrochloric acid (sp. gr. 1.19). Dissolve the aluminum chloride from the filter with a small amount of hot water, and reprecipitate with hydrogen chloride as before. Combine the two filtrates and evaporate to small volume. If the sample was five grams, make another ether-hydrochloric acid separation to avoid an excessive amount of precipitate in the latter separations. Add 5 ml. of 1 : 3 sulfuric acid and evaporate to fumes. Add a little water, boil to solution of salts, filter off the silica, and wash the paper well.

Separation from Iron, Aluminum and Titanium.—To the filtrate add 2 drops of rosolic acid indicator, and neutralize with the solution of ammonium hydroxide. Boil briefly and filter. Wash twice with hot slightly ammoniacal 1% ammonium chloride. Dissolve the precipitate with hot 1 : 1 hydrochloric acid, dilute to 100 ml. and reprecipitate as before. Filter and wash with the

[5] Method of the Aluminum Company of America, Aluminum Research Laboratories. Standard Method Analysis of Aluminum and Aluminum Alloys, by H. V. Churchill, Chief Chemist.

solution previously used. Dissolve this precipitate in hot 1 : 1 hydrochloric acid and wash the paper well. Neutralize with ammonium hydroxide to methyl red and make just acid with hydrochloric acid. Warm the solution to 60° C. and add an excess of 8-hydroxyquinoline. Add 2N ammonium acetate until iron, aluminum, and titanium are precipitated, and add 25 ml. excess. An excess of 8-hydroxyquinoline is indicated by the yellow color of the supernatant liquid after the precipitate has settled. Filter and wash with cold water four times.

Precipitation of Beryllium.—Heat the filtrate to 60° C., and add ammonium hydroxide until the solution is alkaline to methyl red indicator, then add 2 ml. in excess. Allow to cool and filter, using suction. Wash four times with water containing 1% ammonium acetate.

Place in a weighed porcelain crucible provided with a lid. Dry and ignite at 500° C. until the paper is burned off, then at 1000° C. for an hour. Cover the crucible and cool in a sulfuric acid or activated alumina desiccator. When cool, weigh as quickly as possible with the crucible still covered. The gain in weight of the crucible represents beryllium oxide.[7]

TANNIC ACID METHOD

Dilute the slightly acid solution containing not more than 0.1 gram of beryllium oxide to 300–400 ml. of solution, add 20–30 grams of ammonium nitrate, and heat to boiling. Add about ten molecules of tannic acid for each molecule of beryllium oxide and, while stirring, add ammonium hydroxide dropwise until no more precipitation takes place. Should alkali cation be present, and no other foreign one is permissible, dissolve the washed precipitate in a little hydrochloric acid or sulfuric acid and repeat the precipitation. Dry at 110° C., ignite after moistening the filter with nitric acid and weigh as beryllium oxide. This method is very satisfactory for determining small quantities of beryllium.

In order to separate the beryllium from metals whose ions are precipitated by tannic acid, the following procedures are given:

1. **Beryllium from Ferric Iron.**—To the neutralized solution of iron and beryllium add 30–40 grams of ammonium acetate and 20–25 grams of ammonium nitrate. Dilute to 400–500 ml. and, for each 100 ml. of solution, add 1.5 ml. of 80% acetic acid. Heat to boiling and while stirring add 10% tannin solution until the precipitation of the iron is complete. Since the tannin is likely to reduce some of the iron, it is well to add a few drops of 3% hydrogen peroxide just prior to the addition of the tannin. Filter and wash with hot water. Dissolve the precipitate in hot dilute sulfuric acid and repeat the precipitation of the iron by the addition of ammonium acetate, ammonium nitrate, and acetic acid. In the combined filtrates, precipitate beryllium hydroxide by adding ammonium hydroxide, etc.

[7] Preparation of Reagents.—To prepare the 8-hydroxyquinoline solution, triturate 5 grams of the solid reagent with 10 ml. of glacial acetic acid, and when completely dissolved pour into 200 ml. of water heated to 60° C. One milliliter of this solution will precipitate 2.9 mg. of alumina and approximately equal amounts of ferric and titanium oxides.

To prepare rosolic acid indicator solution, dissolve 0.080 grams of the solid in 100 ml. of 1 : 1 ethyl alcohol.

2. Beryllium from Chromium.—The separation takes place as with iron in the presence of about 2% of free acetic acid.

3. Beryllium from Titanium.—The fiery-red titanium adsorption compound is insoluble in strong acetic acid. Add ammonium hydroxide to the acid solution until precipitation starts, then add 10 grams of ammonium acetate, 20 grams of ammonium nitrate, and 20–25 ml. of 80% acetic acid. Heat to boiling, add a ten-fold excess of tannin, boil a little longer and filter. The separation is in this case complete the first time.

4. Beryllium from Zirconium.—The separation is the same as with titanium, but the precipitate is white in this case.

5. Beryllium from Thorium.—Here also the precipitate is white. The separation succeeds in 2–2.5% of acetic acid but the precipitation must be repeated.

6. Beryllium from Tungsten.—In this case the precipitation of the last traces of tungsten requires longer heating, so the filtrate must be allowed to stand on the water bath for several hours to accomplish the precipitation of the last traces of tungsten.

7. Beryllium from Vanadium.—In this case there is partial reduction of vanadate to vanadyl salt by the tannin, but the deep blue voluminous vanadium precipitate is practically insoluble in acetic acid. The conditions recommended are as with iron except that 2.5 ml. of 80% acetic acid should be present in 100 ml. of solution, and one precipitation only is necessary.

THE DETECTION OF TRACES OF BERYLLIUM AND THE COLORIMETRIC DETERMINATION OF THIS ELEMENT

Recently[8] it has been shown that adsorption indicators can be used advantageously for the detection and colorimetric determination of some elements. As is well known, there are only a very few characteristic reactions for beryllium, and only two color reactions have been described in the literature.

1, 2, 5, 8-Oxyanthraquinone as Indicator (0.1% solution in alcohol).—To 10 ml. of the solution, 0.1 ml. indicator and 6 to 8 drops of 4 N ammonia are added, the mixture is boiled and the color observed after five minutes' standing.

A solution containing 500 mg. of beryllium in a liter gives a flock with dark blue color; the supernatant liquid is colorless. With 50 mg. of beryllium per liter, the lake is violet blue; with 5 mg. of beryllium per liter no lake is formed; the solution has a blue-violet color.

A blank without beryllium gives a violet color; if the color of the unknown is compared with that of the blank, 0.5 mg. of beryllium per liter may be detected by the blue-violet color.

In the presence of ammonium chloride, the sensitivity is not changed, the lake formed settling out much sooner. Ten ml. of solution with 0.1 ml. of indicator, 1 ml. of 4 N ammonium chloride and 6 to 8 drops of 4 N ammonia are boiled and observed after five minutes. Five mg. of beryllium per liter gives a flock with a blue-violet color. More dilute solutions only give a blue-violet color (as without ammonium chloride); after standing

[8] I. M. Kolthoff, J. Am. Chem. Soc., 50, 393, 1928.

overnight the lake flocculates with the same shade. In this way even 0.5 mg. of beryllium per liter can be detected. Aluminum, which very often occurs in the presence of beryllium, interferes. It forms a violet lake with the dyestuff and in the presence of excess aluminum the blue-violet color of the beryllium lake can no longer be seen. The aluminum has to be removed (see below).

Unfortunately, the blank without beryllium gives a solution with a violet color, and for this reason it is hard to apply the reaction described for a colorimetric determination of the element. Therefore a search was made for some other reagent more suitable for this purpose.

Curcumin as Reagent (0.1% solution in alcohol).—In weakly alkaline solution, this indicator is adsorbed by the beryllium hydroxide with the formation of an orange-red color.

To 10 ml. of solution are added 1 drop of indicator (no more), 0.5 ml. of 4 N ammonium chloride and 6 to 8 drops of 4 N ammonia.

A solution containing 50 mg. of beryllium per liter gives a flocculent precipitate with a red color; with 1 mg. of beryllium per liter the color is orange-red. If the color is compared with that of a blank, the sensitivity may be increased to 0.05 mg. of beryllium per liter. The color of the blank is yellow-brown.

The appearance of the solution changes on standing, as the lake flocculates. After standing overnight, the adsorption compound sinks to the bottom of the test-tube and may be detected by its color (orange-red).

The reaction is very suitable for the quantitative colorimetric determination of beryllium in concentrations between 1 and 0.05 mg. per liter. If the color is compared with solutions of known beryllium content after the *same time of standing*, the method gives good results. Not more than 0.5 to 1 ml. of 4 N ammonium chloride should be added to 10 ml. of solutions; otherwise the sensitivity is decreased.

Potassium, sodium, lithium, calcium and barium do not interfere. Magnesium decreases the sensitivity somewhat, but 1 mg. of beryllium per liter in the presence of 1 g. of magnesium per liter can be detected in the way described.

Aluminum has a disturbing effect as it also forms a colored lake. For the detection of aluminum this reaction, however, is not very suitable. If beryllium is to be detected in the presence of aluminum, the slightly acid solution is treated with an excess of sodium fluoride. The main part of aluminum precipitates in the form of Na_3AlF_6, and the rest in solution does not interfere. After standing for one hour, the liquid is filtered and the filtrate treated in the way described above. One mg. of beryllium per liter could be detected in the presence of 1 g. of aluminum per liter. We may remark here that sodium fluoride decreases the sensitivity of the reaction for beryllium somewhat.

Ferric iron interferes and can be made harmless in the same way as described for aluminum. Or, more easily still, the iron may be precipitated at room temperature with an excess of sodium hydroxide, and 1 drop of curcumin and an excess of ammonium chloride added to the filtrate. Two mg. of beryllium per liter in the presence of 1 g. of iron per liter could be easily seen.

It may be mentioned here that in strong alkaline solutions beryllium does not react with the curcumin (the beryllium hydroxide dissolves again).

Under these conditions magnesium gives a distinct color reaction, which, however, is not as sensitive as that with titan yellow.

VOLUMETRIC METHODS

QUINALIZARIN COLORIMETRIC TITRATION

Quinalizarin (1, 2, 5, 8-tetrahydroxyanthraquinone) is a sensitive reagent for detecting beryllium. By means of it, as little as 0.03% beryllium in aluminum can be recognized. Aluminum interferes only when present together with tartrate. Magnesium gives a similar test but its lake can be distinguished from the beryllium lake in two ways: in sodium hydroxide solution, Br_2 water destroys the latter but not the former; in ammonium hydroxide solution Br_2 water bleaches the former but not the latter.

Procedure.—Iron in quantity exceeding that of beryllium interferes with the quinalizarin colorimetric titration of beryllium. To separate beryllium from large quantities of iron both metals are precipitated with ammonia from a cold solution. The precipitate is collected, washed, dried, and ignited over a blast. The mixed oxides are reduced in hydrogen, and the metallic iron is extracted with hydrochloric acid. Strongly ignited beryllia is insoluble in all acids except hydrofluoric acid. The residue is therefore dissolved in warm hydrofluoric acid, the solution treated with sodium hydroxide to 0.25 N, and titrated colorimetrically with quinalizarin. Compare the color with that obtained in a blank test; sodium hydroxide alone gives a violet color whereas the beryllium test is blue.

To determine beryllium in copper, nickel, or zinc alloys, 0.5 grams is dissolved in concentrated hydrochloric acid and a little hydrogen peroxide, the solution evaporated to dryness on the water bath, the residue dissolved in water, and 10% potassium cyanide solution added until the precipitate ceases to dissolve. After addition of 50 ml. of N sodium hydroxide, the solution is diluted to 200 ml. and the beryllium titrated.

For the determination of beryllium in beryl and similar minerals one gram of the finely ground substance is intimately mixed with one gram of Na_2SiF_6 and the mixture heated at 680°–710° C. in a porcelain crucible. The aqueous extract of the product is treated with sodium hydroxide, etc. as described above. Ammonia does not precipitate beryllia completely from fluoride solutions; they must therefore be evaporated with sulfuric acid before addition of ammonia, for the gravimetric determination of beryllia.

Modification.—The addition of a violet alkaline solution of quinalizarin to an alkaline beryllium solution gives a distinct blue precipitate which is suitable for the detection of beryllium in the presence of aluminum, iron, phosphate,

tartrate and magnesium. Small quantities of beryllium can be detected by precipitation as the water-insoluble-beryllium-dye by addition of excess of ammoniacal quinalizarin solution. The beryllium dye is centrifuged off and determined colorimetrically. Small amounts of beryllium can be titrated directly and the end point observed by the color change produced by excess quinalizarin. One molecule of quinalizarin unites with two molecules of beryllium.

In a modification of this method an excess of the alkaline quinalizarin solution is added and the excess titrated back with a known beryllium solution. The end point is ascertained by colorimetric comparison of the solution, which was reddish colored, with a blue solution of the beryllium-dye freed of excess quinalizarin.

THE ANALYSIS OF BERYLLIUM-COPPER ALLOYS *

A. IF ALUMINUM IS NOT PRESENT

Determination of Copper.—In a 400 ml. beaker, dissolve 5 g. of the well mixed drillings that have been treated with a magnet, in 45 ml. of a mixed acid solution (containing 250 ml. conc. H_2SO_4, 175 ml. conc. HNO_3 and 625 ml. distilled water). Dilute to 250 ml. and determine copper by the electrolytic method. Check determinations are to be made.

Determination of Beryllium.—Transfer the solution from one of the copper determinations to a 500 ml. volumetric flask and carefully make up to the mark. Pipette into a 250 ml. beaker 50 ml. of this solution making a 0.5 g. sample for the determination. Add 5 ml. of H_2SO_4 (sp. gr. 1.84) a few drops of hydrofluoric acid and evaporate to fumes of SO_3. Dilute to 125 ml., oxidize with bromine water, add a few drops of phenolphthalein solution and make just ammoniacal. Ignite and blast the precipitate in a covered platinum crucible and weigh the residue as the combined oxides of beryllium and iron. From the iron determination calculate the amount of Fe_2O_3 in the residue and apply the correction, the corrected weight representing BeO. Beryllium shall then be calculated using the factor 0.3605. Check determinations are to be made.

NOTE.—The accuracy of this procedure is such that determinations made by different laboratories should check within the limits of 0.1%.

Determination of Iron.—The solution from the other copper determination shall be transferred to a 500 ml. volumetric flask and carefully made up to the mark. Pipette out two 200 ml. portions into 400 ml. beakers making 2.0 g.

* Supplied through the courtesy of the American Brass Company.

samples for this determination. Add 2 to 3 g. NH_4Cl, oxidize with bromine water and make ammoniacal. Filter through a loosely woven paper and wash with dilute ammonia and hot water. Dissolve the precipitate back into the original beaker with hot 1–1 HCl and wash the paper with hot water. Reprecipitate with ammonia, filter and wash as before, but dissolve the precipitate with hot 1–4 H_2SO_4. With additional sulfuric acid, pass the sample through a Jones reductor, and titrate with standard permanganate solution.

Determination of Nickel.—Acidify the filtrate from the beryllium determination with hydrochloric acid and make just ammoniacal. Add 10 ml. of a 10% alcoholic solution of dimethylglyoxime and allow to stand on the steam bath for 30 minutes. Filter on a closely woven paper and wash thoroughly with hot water that is faintly ammoniacal. Using hot 1–1 hydrochloric acid, dissolve the precipitate through the paper into a 250 ml. beaker and wash the paper with hot water. Add 10 ml. 1–1 H_2SO_4 and take to fumes of SO_3. Destroy organic matter with a few drops of HNO_3 (sp. gr. 1.42) and fume again. After cooling, add 100 ml. of water and 40 ml. of NH_4OH (sp. gr. .90) and electrolyze, weighing the deposit as metallic nickel.

Determination of Silicon.—In a 300 ml. porcelain casserole, dissolve 5 g. of the metal in a mixture of 10 ml. H_2SO_4 (sp. gr. 1.84), 10 ml. HNO_3 (sp. gr. 1.42) and 30 ml. water. Evaporate to sulphuric acid and fume strongly for several minutes. Take up with 100 ml. of water containing 10 ml. HCl (sp. gr. 1.2), and bring to a boil and filter through a closely woven ashless paper. Wash thoroughly with hot water, ignite the residue in a platinum crucible and weigh. Moisten the residue with a few drops of 1–1 H_2SO_4, add 4–5 ml. H_2F_2 and evaporate to dryness. Ignite the crucible at a dull red heat for five minutes, cool, and reweigh. The loss in weight is SiO_2.

B. IF ALUMINUM IS PRESENT

Solutions Required for Determination of Beryllium and Aluminum.—***8-hydroxyquinoline solution:*** Triturate 2.5 grams of the solid reagent with 5 ml. of glacial acetic acid; when completely dissolved pour into 100 ml. H_2O and heat to 60° C. 1 ml. will precipitate 2.9 mg. of alumina and approximately equal quantities of ferric and titanium oxides.

Ammonium Chloride Solution for Washing: Dissolve 10 grams NH_4Cl in H_2O, make just alkaline with NH_4OH and dilute to 1000 ml.

Ammonium Acetate 2N Solution: Dissolve 15.4 grams $NH_4C_2H_3O_2$ in H_2O and dilute to 100 ml.

Method

Pipette 100 ml. of the solution from the copper determination that has been made up to 500 ml. into a 250 ml. beaker making a 1 g. sample for the determination. Add a few drops of hydrofluoric acid, 5 ml. of H_2SO_4 (sp. gr. 1.84) and evaporate to fumes of SO_3. Allow to cool, dilute to 125 ml. and oxidize with bromine water, boiling off all excess. Add a few drops of phenolphthalein solution, make just ammoniacal, boil one minute and filter. Wash beaker twice and precipitate twice with the hot 1% ammonium chloride solution for washing. Dissolve the precipitate with hot 1–1 hydrochloric acid and wash papers thoroughly with hot H_2O. Dilute to 100 ml. add a few drops methyl red

indicator and neutralize with NH_4OH, then add HCl dropwise until the solution is acid and clear. Heat to 60° C. and add an excess of 8-hydroxyquinoline; 10–15 ml. is usually sufficient. Add 2N Ammonium Acetate Solution until all the aluminum and iron are precipitated, then 25 ml. excess. An excess of 8-hydroxyquinoline is indicated by the yellow color of the supernatant liquid. Filter and wash six times with cold water. Reserve the filtrate for the determination of beryllium. The precipitate containing the iron and aluminum is dissolved back into the original beaker with hot 1–1 HCl and the paper washed thoroughly with hot H_2O. Add 10 ml. 1–1 H_2SO_4 and evaporate to fumes of SO_3; destroy any organic matter with additions of concentrated HNO_3. The solution is now taken up with 75 ml. of water, two drops of methyl red are added, and it is made just alkaline with NH_4OH. Boil one minute and filter on ashless paper. Police the beaker and wash the precipitate with 1% ammonium chloride solution. Ignite the precipitate containing iron and aluminum hydroxide in a weighed platinum crucible and record the weight. Now add about 5 grams of fused potassium bisulphate and fuse, slowly at first, then gradually to red heat. Cool, dissolve fusion in hot water adding about 10 ml. H_2SO_4 1–1. After solution is cool, pass through a Jones reductor and titrate the iron with $\frac{N}{100}$ $KMnO_4$, calculate to % iron in sample, also calculate to grams Fe_2O_3 and subtract from combined weight of $Al_2O_3+Fe_2O_3$. From the Al_2O_3 thus obtained, calculate to % Al in sample. Heat the filtrate containing the beryllium to 60° C. and add NH_4OH until alkaline to phenolphthalein. Allow to cool and filter on ashless paper, police beaker and wash precipitate with 1% ammonium acetate solution. Ignite in a weighed platinum crucible, provided with a cover. Dry at 500° C. until paper is burned off, then at 1000° C. for one hour. When cool, weigh as quickly as possible with crucible still covered and record as BeO.

$$\frac{\text{BeO}\times 0.3605\times 100}{\text{Weight of Sample}} = \%\ \text{Beryllium}$$

NOTES.—1. The limit of Al present that can be conveniently determined by this method appears to be about 25 mg.

2. If much iron and (or) aluminum is present, repeat the precipitation with hydroxyquinoline combining the filtrates for the beryllium determination.

Other Methods.—A description of the various volumetric and physicochemical methods cannot be undertaken here. The following bibliography should be of assistance in this connection.

1. DIXON, B. E., Analyst, **54**, 268–274 (1929). C. A., **23**, 4636 (1929).
2. HOPKINS, Chemistry of the Rarer Elements, pp. 82–85.
3. MELLOR, J. W., Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. IV, 204–210.
4. Ind. and Eng. Chem., Anal. Ed. **2**, 405–407 (1931).
5. BROWNING, Introduction to the Rarer Elements, pp. 17–22.
6. PARSONS AND BARNES, J. Am. Chem. Soc., **28**, 1589–1595 (1906).
7. BRITTON, H. T. S., J. Chem. Soc., **127**, 2110–20 (1925).
8. CAGLIOTTI, V., C. A., **22**, 1300 (1928).
9. FISCHER, HELLMUT, Z. anal. Chem., **73**, 54–64 (1928). C. A., **21**, 1806.
10. FESEFELDT, H., Z. physik. Chem., 140 (1929). C. A., **23**, 2652–3.
11. FRESENIUS, L., AND FROMMES, M., Z. anal. Chem., **87**, 273 (1932).
12. FROMMES, M., Z. anal. Chem., **93**, 285–307 (1932). Review of literature. See also ibid., **93**, 275 (1932).
13. EVANS, B. S., Analyst, **60**, 291 (1935).

BISMUTH[1]

Bi, *at.wt.* 209.0; *sp.gr.* 9.7474; *m.p.* 271°; *b.p.* 1450° C.; *oxides*, Bi_2O_3, Bi_2O_5

Bismuth is not an abundant element. It occurs free in nature and combined as oxides and sulfides (bismuthinite). It is found combined as arsenate, carbonate, molybdate, oxide, telluride, silicate and vanadate. In small quantities it is found in conjunction with copper, cobalt, arsenic, lead, nickel, molybdenum, silver, tin, vanadium. The principal source in the United States is from the residues of lead refining.

DETECTION

Bismuth is precipitated from its solution, containing free acid, by H_2S gas, as a brown sulfide, Bi_2S_3. The compound is insoluble in ammonium sulfide (separation from arsenic, antimony, and tin), but dissolves in hot dilute nitric acid (separation from mercury). The nitrate, treated with sulfuric acid and taken to SO_3 fumes, is converted to the sulfate and dissolves upon dilution with water (lead remains insoluble as $PbSO_4$). Bismuth is precipitated from this solution by addition of ammonium hydroxide, white $Bi(OH)_3$ being formed (copper and cadmium dissolve). If this hydroxide is dissolved with hydrochloric acid and then diluted with a large volume of water, the white, basic salt of bismuth oxychloride, $BiOCl$, is precipitated. The compound dissolves if sufficient hydrochloric acid is present. It is insoluble in tartaric acid (distinction from antimony).

Reducing Agents.—Formaldehyde in alkaline solution, hypophosphorous acid, potassium or sodium stannite, reduce bismuth compounds to the metallic state. For example, a hot solution of sodium stannite poured onto the white precipitate of $Bi(OH)_3$ on the filter will give a black stain. The test is very delicate and enables the detection of small amounts of the compound.

$$3K_2SnO_2+2BiCl_3+6KOH=2Bi+3K_2SnO_3+6KCl+3H_2O.$$

[1] Bismuth was known during the Middle Ages, although it was confused, frequently, with tin, lead, antimony and zinc. Parcelsus named the element "wissmat" which later became latinized "bisemutum." The metal is used in the preparation of alloys of low melting point, which are characterized by their expansion on cooling. The compounds are used for medical purposes, the sub-nitrate being especially useful. The salts are generally not poisonous and may be taken internally without danger.

Blowpipe Test.—A compound of bismuth heated on charcoal with a powdered mixture of carbon, potassium iodide and sulfur, will give a scarlet incrustation on the charcoal.

ESTIMATION

The determination of bismuth is required in complete analysis of ores of cobalt, nickel, copper, silver, lead, and tin, in which it is generally found in small quantities, and in the evaluation of bismuthite, bismuth ochre, etc. Bismuth is often determined in the analysis of such minerals as molybdenite and wolframite. It is determined in the residues from the refining of lead (the principal source of bismuth in the United States), in alloys—antifriction metals, electric fuses, solders, stereotype metals, certain amalgams used for silvering mirrors (with or without lead or tin), and in bismuth compounds.

In general methods of analysis of ores it must be kept in mind that bismuth is apt to be left with the silica residue as an oxycompound. Unless taken care of a portion may pass into the ammonium sulfide group where it is precipitated with aluminum causing an error in its determination. Bismuth deposites both on the anode and cathode in electrolysis and is apt to contaminate copper in its electrolytic determination.

For determination of bismuth the ore is decomposed by treatment with HNO_3, followed by HCl and finally H_2SO_4 taking to fumes. After extracting the greater part of bismuth with water, the residue is fused with Na_2CO_3, SO_4 and silicate leached out with water and the bismuth recovered from the residue by dissolving in HNO_3 and converting to BiOCl.

PREPARATION AND SOLUTION OF THE SAMPLE

In dissolving the substance, the following facts must be kept in mind. Nitric acid is the best solvent of the metal. Although it is soluble in hot sulfuric acid, it is only very slightly soluble in the cold acid. The metal is practically insoluble in hydrochloric acid, but readily dissolves in nitrohydrochloric acid. The hydroxides, oxides, and most of the bismuth salts are readily soluble in hydrochloric, nitric, and sulfuric acids.

Ores or Cinders.—One gram of the finely pulverized ore or cinder (or larger amounts where the bismuth content is very low) is treated in a 400-ml. beaker with 5 ml. of bromine solution ($Br+KBr+H_2O$),[2] followed by the cautious addition of about 15 ml. of HNO_3 (sp.gr. 1.42). When the violent action has ceased, which is apt to occur in sulfide ores, the mixture is taken to dryness

[2] Bromine solution is made by dissolving in water 75 grams of KBr, to which are added 50 grams of liquid bromine and the mixture diluted to 500 ml. with water.

on the steam bath, 10 ml. of conc. HCl and 20 ml. of concentrated H_2SO_4 added and the covered sample heated until SO_3 fumes are freely evolved. The cooled solution is diluted with 50 ml. of water and gently heated until only a white or light gray residue remains. The solution is filtered and the residue washed with dilute H_2SO_4 (1 : 10), to remove any adhering bismuth. Silica, the greater part of the lead (also $BaSO_4$) remain in the residue, whereas the bismuth, together with iron, alumina, copper, antimony, etc., are in the solution. Details of further treatment of the solution to effect a separation of bismuth are given under "Separations" and in the procedures for the determination of bismuth.

Alloys, Bearing Metal, etc.—One gram of the borings, placed in a small beaker, is dissolved by adding 20 ml. of concentrated HCl and 5 ml. of conc. HNO_3. The alloy will usually dissolve in the cold, unless considerable lead is present, in which case prolonged heating on the steam bath may be necessary. (A yellow or greenish-yellow color at this stage indicates the presence of copper.) Lead may now be removed either as a sulfate by taking to SO_3 fumes with H_2SO_4 or by precipitating as chloride, in the presence of alcohol, according to directions given under "Separations." The bismuth is determined in the filtrate from lead according to one of the procedures given later.

Lead Bullion, Refined Lead.—Ten to twenty-five grams of the lead, hammered or rolled out into thin sheets and cut into small pieces, are taken for analysis. The sample is dissolved by a mixture of 250 ml. of water and 40 ml. of conc. nitric acid, in a large covered beaker, by warming gently, preferably on the steam bath. When the lead has dissolved, the beaker is removed from the heat and dilute ammonia (1 : 2) added to the warm solution, very cautiously and finally drop by drop until the free acid is neutralized and the liquid remains faintly opalescent, but with no visible precipitate. Now 1 ml. of dilute HCl (1 : 3) is added. The solution will clear for an instant and then a crystalline precipitate of bismuth oxychloride will form, if any considerable amount of bismuth is present. The beaker is now placed on the steam bath for an hour, during which time the bismuth oxychloride will separate out, together with a small amount of lead and with antimony if present in appreciable amounts. The further isolation and purification of bismuth is given under "Separations." In brief—antimony is removed by dissolving the precipitate in a small amount of hot dilute HCl (1 : 3), precipitating bismuth, traces of lead, and the antimony by H_2S, dissolving out the antimony sulfide with warm ammonium sulfide, dissolving the Bi_2S_3 and PbS in HNO_3 and reprecipitating the bismuth according to the procedure given above. Bismuth is now determined as the oxychloride. Further details of this method are given under the gravimetric procedures for bismuth.

SEPARATIONS

The following procedures are given in the order that would be followed in the complete analysis of an ore in which all the constituents are sought. This general scheme, however, is not required for the majority of bismuth-bearing samples commonly met with in the commercial laboratory, direct precipitations of bismuth frequently being possible.

Separation of Bismuth from Members of Subsequent Groups, Fe, Cr, Al, Mn, Co, Ni, Zn, Mg, the Alkaline Earths and Alkalies, Together with Rare Elements of these Groups.—The solution should contain 5 to 7 ml. of concentrated hydrochloric acid (sp.gr. 1.19) for every 100 ml. of the sample. The elements of the hydrogen sulfide group are precipitated by saturating the solution with H_2S (Hg, Pb, Bi, Cu, Cd, As, Sb, Sn, Mo, Se, Te, Au, Pt). The members of subsequent groups remain in solution and pass into the filtrate.

Separation of Bismuth from Arsenic, Antimony, Tin, Molybdenum, Tellurium, Selenium.—In presence of mercury, the soluble members of the hydrogen sulfide group are separated from the insoluble sulfides by digesting the precipitate above obtained with ammonium sulfide. Arsenic, antimony and tin sulfides dissolve. Bismuth sulfide remains insoluble (as do Hg, Pb, Cu, Cd).

Separation of Bismuth from Mercury.—The insoluble sulfides, remaining from the above treatment with ammonium sulfide after being washed free of the soluble members of this group, are placed in a porcelain dish and boiled with dilute nitric acid (sp.gr. 1.2 to 1.3). The solution thus obtained is filtered, upon dilution, from the insoluble sulfide of mercury. A little of the lead may remain as $PbSO_4$, the solution may contain lead, bismuth, copper, and cadmium.

Separation of Bismuth from Lead.—This is the most important procedure in the determination of bismuth as the separation is almost invariably necessary, since these elements commonly occur together.

Oxy-Bromide Method for Separating Bismuth.—The usual procedure for a preliminary separation of lead as $PbSO_4$ does not effect a complete separation from bismuth as this will in part be carried down with the lead sulfate. The method recommended by L. Moser and W. Maxymowicz (Z. anal. Chem., **67**, 248, 1925–26) is the Oxy-Bromide Method, which also effects a separation of bismuth from copper, cadmium, zinc as well as the lead.

The nitric acid solution containing the elements in question (free from chlorides and ammonium salts[3]) is carefully neutralized by addition of small portions at a time of sodium carbonate solution until the precipitate that forms dissolves tardily. The solution diluted to about 300 ml. is treated with 2–3 g. of potassium or sodium bromate ($KBrO_3$ or $NaBrO_3$) and heated to boiling. If the solution becomes cloudy it is cleared with a few drops of HNO_3. To the hot solution is now added a 10% solution of KBr or NaBr dropwise from a pipette until the solution becomes turbid, the solution being colored brown by free bromine. It is now boiled until a clear yellow color is obtained. More bromide is added and the solution is again boiled as before. This is repeated as long as a precipitation occurs with the addition of the bromide. Additional bromate at this stage will cause no further precipitation. The bromine is expelled by boiling and the precipitate filtered off. It is advisable to dissolve the precipitate in HNO_3 and repeat the precipitation to completely eliminate lead etc. The precipitate is BiOBr.

Separation of Bismuth as the Oxy-Chloride.—See under Methods.

Separation of Bismuth from Copper and Cadmium. This separation is accomplished by precipitating bismuth as the oxychloride by hydrolysis, or as the carbonate by adding a slight excess of ammonium carbonate to

[3] Ammonium salts retard precipitation.

the solution nearly neutralized by ammonia, or as the hydroxide by adding an excess of ammonia. Details of these procedures are given under the gravimetric methods for determining bismuth.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF BISMUTH

DETERMINING SMALL AMOUNTS OF BISMUTH BY PRECIPITATION AND WEIGHING AS THE BASIC CHLORIDE, BiOCl[4]

The determination depends upon the formation of the insoluble oxychloride, BiOCl, when a hydrochloric acid solution of bismuth is sufficiently diluted with water, the following reaction taking place, $BiCl_3+H_2O=BiOCl+2HCl$.

The procedure is recommended for the determination of bismuth in refined lead, bearing metal, and bismuth alloys. Copper, cadmium, and lead do not interfere; appreciable amounts of antimony and tin, however, should be removed by H_2S precipitation and subsequent treatment with $(NH_4)_2S$ and the residual sulfides dissolved in hot dilute nitric acid, according to directions given under "Separations." Silver, mercurous mercury, thallium, zirconium should be absent.

Properties.—BiOCl, *mol.wt.*, 260.46; *sp.gr.*, 7.717$^{15°}$; *m.p.*, red heat; *insol. in* H_2O *and in* $H_2C_4H_4O_6$, *soluble in acids; white quadratic crystals.*

Procedure.—The solution of bismuth, freed from appreciable amounts of tin and antimony, is warmed gently and treated with sufficient ammonia to neutralize the greater part of the free acid. At this stage a precipitate is formed which dissolves with difficulty; the last portion of the dilute ammonia (1 : 2) is added drop by drop, the solution is diluted to about 300 ml., and the remainder of the free acid neutralized with dilute ammonia added cautiously until a faint opalescence appears, but not enough to form an appreciable precipitate. One to 3 ml. of dilute hydrochloric acid (1 part HCl sp.gr. 1.19 to 3 parts H_2O) are now added, the mixture stirred and the bismuth oxychloride allowed to settle for an hour or so on the steam bath, then filtered hot by decanting off the clear solution through a weighed Gooch crucible. The precipitate is washed by decantation twice with hot water and finally washed into the Gooch, then dried at 100° C. and weighed as BiOCl.

$$BiOCl\times 0.8024=Bi.$$

NOTE.—Three ml. of dilute hydrochloric acid (or 1 ml. conc. HCl, sp.gr. 1.19) are sufficient to precipitate completely 1 gram of bismuth from solution.

[4] The method is best suited to amounts of bismuth below 10 mg.

DETERMINATION OF LARGE AMOUNTS OF BISMUTH AS THE OXIDE, Bi_2O_3[5]

Preliminary Considerations.—The determination of bismuth as the oxide requires the absence of hydrochloric acid or sulfuric acid from the solution of the element, since either of these acids invariably contaminates the final product. In presence of these acids, which is frequently the case, determination of bismuth by precipitation as Bi_2S_3 or by reduction to the metal and so weighing is generally recommended; a brief outline of the methods is given later. A solution of bismuth free from hydrochloric acid and practically free of sulfuric acid may be obtained by precipitating Bi_2S_3, together with CuS, CdS, and PbS, and dissolving the sulfides in nitric acid, the amount of sulfuric acid formed by the reaction being negligible.

Two general conditions will be considered: 1. *Solutions containing lead Copper and cadmium may also be present.* 2. *Solutions free from lead* Copper and cadmium may be present.

1. Separation from Lead, Copper, and Cadmium, by Precipitation as Basic Nitrate.[6]—Either the sulfuric or hydrochloric acid methods may be employed for effecting the separation of lead by precipitation Furthermore advantage may be taken of the fact that bismuth nitrate is changed by the action of water into an insoluble basic salt, while lead, copper, and cadmium do not undergo such a transformation.

Procedure. -The bismuth nitrate solution is evaporated to syrupy consistency and hot water added with constant stirring with a glass rod. The solution is again evaporated to dryness, and the hot-water treatment repeated. Four such evaporations are generally sufficient to convert the bismuth nitrate completely into the basic salt; when this stage is reached the addition of water will fail to produce a turbidity. The solution is finally evaporated to dryness and, when free from nitric acid, is extracted with cold ammonium nitrate solution (1 $NH_4NO_3 : 500\ H_2O$) to dissolve out the lead and other impurities. After allowing to stand some time with frequent stirring, the solution is filtered and the residue washed with ammonium nitrate solution, then dried.

Ignition to Bismuth Oxide.- As much of the precipitate as possible is transferred to a weighed porcelain crucible, the filter is burned and the ash added to the main precipitate. This is now gently ignited over a Bunsen burner. Too high heating will cause the oxide to fuse and attack the glaze of the crucible.

Properties. --$Bi(OH)_2NO_3$, *mol.wt.*, 305.02; *sp.gr.*, $4.928^{15°}$; *decomp.*, 260°; *insol. in* H_2O; *sol. in acids; hexagonal plates.*

Bi_2O_3, *mol. wt.*, 466.0; *sp.gr.*, 8.8 *to* 9.0; *m.p.*, 820 to 860°; *insoluble in cold water and in alkalies, but soluble in acids; yellow tetragonal crystals.*

$$Bi_2O_3 \times 0.8970 = Bi.$$

2. Precipitation of Bismuth as the Subcarbonate or Hydroxide, Lead being Absent.—Either of these procedures effects a separation of bismuth from copper and cadmium.

[5] Amounts over 10 mg.
[6] J. Löwe, J. prak. Chem. (1), 74, 344, 1858.

A. Procedure. Precipitation as the Subcarbonate.—[illegible] to about 200 ml. [illegible] which [illegible] is obtained [illegible] excess of ammonium carbonate. The solution is heated to boiling, the precipitate filtered off, washed with hot water, dried and ignited according to directions given in the bismuth subnitrate method. The residue is weighed as Bi_2O_3.

B. Procedure. Isolation of Bismuth by Precipitation as the Hydroxide.[7]—The solution is taken to dryness and the residue treated with 5 ml. of nitric acid (1 : 4) and 25 ml. of water added. The resulting solution is poured, with constant stirring, into 25 ml. of concentrated ammonia and 50 ml. of 4% hydrogen peroxide. Upon settling of the bismuth hydroxide, the clear solution is filtered off and the residue is treated with more ammonia and peroxide. It is then filtered onto a filter paper, washed with hot, dilute ammonium hydroxide, (1 : 8), followed by hot water and washed free of any adhering copper or cadmium (no residue when a drop is evaporated on platinum foil). Re-solution in hot dilute nitric acid and reprecipitation may sometimes be necessary to obtain the pure product. The hydroxide may be dried, ignited and weighed as Bi_2O_3 according to directions already given on page 154.

Properties.—$Bi_2O_3 \cdot CO_3 \cdot H_2O$, *mol.wt.*, 544.03; *sp.gr.*, 6.86; *decomp. by heat; insoluble in water, soluble in acids, insoluble in* Na_2CO_3; *white precipitate.*

$Bi(OH)_3$, *mol.wt.*, 260.02; *loses* $1\frac{1}{2}$ H_2O *at* 150°; *insol. in cold water and in alkalies; soluble in acids; white precipitate.*

DETERMINATION OF BISMUTH AS THE SULFIDE, Bi_2S_3

The procedure is applicable to the determination of bismuth in a hydrochloric or sulfuric acid solution, freed from other members of this group.

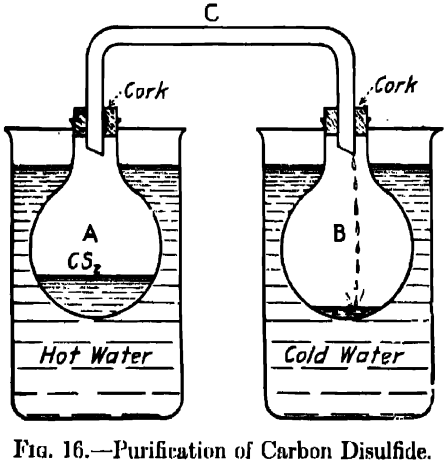


FIG. 16.—Purification of Carbon Disulfide.

Procedure.—Bismuth sulfide is precipitated by passing H_2S into the slightly acid solution, preferably under pressure. When the precipitation is complete,

[7] P. Jannasch, Z. anorg. Chem., 8, 302, 1895.

the bismuth sulfide, Bi_2S_3, is filtered off into a weighed Gooch crucible, the precipitate washed with H_2S water, then with alcohol to remove the water, followed by carbon disulfide to dissolve out the precipitated sulfur, then alcohol to remove the disulfide, and finally with ether. After drying for fifteen to twenty minutes, the residue is weighed as Bi_2S_3. This weight multiplied by 0.8130 = Bi.

NOTE.—The carbon disulfide used should be freshly distilled. This may be accomplished by placing the carbon disulfide in a small flask (*A*, Fig. 16) connected by means of a glass-tube (*C*) to a second flask (*B*), cork stoppers being used. The vessels are immersed in beakers of water, the container with the reagent being placed in hot water (60–80° C.) and the empty flask in cold water. The reagent quickly distills into the empty flask in pure form.

Properties of Bismuth Sulfide.—Bi_2S_3, *mol.wt.*, 514.18; *sp.gr.*, 7–7.81; *decomposed by heat, solubility* = 0.000018g. *per* 100 ml. *cold* H_2O; *soluble in nitric acid; brown rhombic crystals.*

DETERMINATION OF BISMUTH AS THE METAL

Reduction with Potassium Cyanide.[8]—Bismuth precipitated as the carbonate and ignited to the oxide according to the procedure given, is fused in a weighed porcelain crucible with 5 times its weight of potassium cyanide over a low flame. The cooled melt is extracted with water, pouring the extracts through a filter that has been dried and weighed with the crucible. Bismuth is left undissolved as metallic bismuth. After washing with water, alcohol, and ether, the filter, with the metal and loosened pieces of porcelain glaze, is dried at 100° C. together with the crucible. These are then weighed and the increased weight taken as the amount of bismuth present in the sample.

ELECTROLYTIC DEPOSITION OF BISMUTH

With samples containing less than 0.03 gram bismuth, the metal may be satisfactorily deposited by electrolysis of its sulfuric acid solution, lead having been removed previously by sulfuric acid by the standard procedure. The solution should contain about 6 ml. of conc. sulfuric acid per 100 ml. This is electrolyzed with a current of 0.6 to 0.7 ampere and about 2.7 to 3 volts.

Other Methods.—Bismuth may be precipitated quantitatively by adding a solution of $K_3Cr(CNS)_6$ (blue-violet) to a solution that is 0.3 to 1 N in HNO_3. The precipitate is brick-red and has the formula $BiCr(CNS)_6$ after drying at 120–130° C.[9] The method is best applied with amounts of bismuth ranging from 50–125 mg. It serves to separate bismuth from Cr, Mo, Al, Fe^{II}, Zn, Mn, Ni, Co, the alkaline earths, Mg, and the alkalies.

[8] Method by H. Rose, Pogg. Ann., **110**, p. 425.
Vanino and Treubert (Ber., 31, 1303, 1898) reduce bismuth by adding formaldehyde to its slightly acid solution and then making strongly alkaline with 10% NaOH solution and warming.

[9] C. Mahr, Z. anorg. allgem. Chem., **208**, 313 (1932); Montequi and Carrero, C. A., **27**, 2903 (1933).

Bismuth may be converted into complex iodide or bromide ions like BiI_4^-, $BiBr_6^{\equiv}$, and the latter may be precipitated with suitable cobalt or chromium ammines, or with certain basic organic substances.[10]

Numerous organic precipitants and color tests for bismuth have been proposed.

VOLUMETRIC DETERMINATION OF BISMUTH

DETERMINATION OF BISMUTH BY PRECIPITATION AS OXALATE AND TITRATION BY POTASSIUM PERMANGANATE[11]

Normal bismuth oxalate, produced by addition of oxalic acid to a nitric acid solution of the element, boiled with successive portions of water, is transformed to the basic oxalate. This may be titrated with potassium permanganate in presence of sulfuric acid.

Procedure. ***Preparation of the Sample.***—One gram of the finely ground sample is treated with 5 to 10 ml. of concentrated nitric acid and digested on the steam bath and finally evaporated to dryness, the residue is taken up with 5 ml. of nitric acid (sp.gr. 1.42)+25 ml. of water, and diluted to 100 ml.

Precipitation of the Oxalate.—About 5 grams of ammonium oxalate or oxalic acid are added and the liquid boiled for about five minutes, the precipitate allowed to settle and the supernatant solution filtered off. The precipitate is boiled twice with 50-ml. portions of water and the washings poured through the same filter. If the filtrate still passes through acid, the washing is continued until the acid is removed and the washings passing through the filter is neutral. The bulk of the basic oxalate precipitate is placed in a beaker and that remaining on the filter paper is dissolved by adding 2 to 5 ml. of hydrochloric acid, 1 : 1, the solution being added to the bulk of the precipitate. This is now warmed until it goes into solution and the liquid is diluted to 250 ml. with hot water. Dilute ammonia is now added until the free acid is neutralized; the resulting precipitate is taken up with dilute sulfuric acid, 1 : 4, added in slight excess. The resulting solution, warmed to 70° C., is titrated with standard potassium permanganate.

$$\text{One ml. } KMnO_4 \text{ N}/10 = 0.01045 \text{ gram Bi.}$$

[10] Berg and Wurm, Ber., **60**, 1664 (1927); Mahr, Z. anal. Chem., **93**, 433 (1933); Spacu et al. ibid., **79**, 196 (1930); **93**, 260 (1933).

[11] The method is rapid and is sufficiently accurate for commercial work. Warwick and Kyle, Chem. News, **75**, 3.

Muir and Robbs, J. Chem. Soc., **41**, 1.

NOTE.—Lead, copper, arsenic, iron, zinc, and tellurium do not interfere. Hydrochloric acid should not be used to dissolve the sample, as it interferes with the oxalate precipitation.

CINCHONINE POTASSIUM IODIDE, COLORIMETRIC METHOD[12]

This method is applicable for the determination of small amounts of bismuth, 0.00003 to 0.00015 gram, in ores and alloys. The procedure depends upon the fact that bismuth nitrate produces a crimson or orange color when its solution is added to a solution of cinchonine potassium iodide, the intensity of the color depending upon the amount of bismuth in the resulting product.

Special Reagents. ***Cinchonine Potassium Iodide Solution.***—Ten grams of cinchonine are dissolved by treating with the least amount of nitric acid that is necessary to form a viscous mass and taking up with about 100 ml. of water. The acid is added a drop at a time, as an excess must be avoided. Twenty grams of potassium iodide are dissolved separately and cinchonine solution added. The resulting mixture is diluted with water to 1000 ml. After allowing the reagent to stand forty-eight hours, any precipitate formed is filtered off and the clear product is ready for use. The reagent preserved in a glass-stoppered bottle keeps indefinitely. It should be filtered free of suspended matter before use.

Standard Bismuth Solution.—One gram of metallic bismuth is dissolved in the least amount of dilute nitric acid (1 : 1) that is necessary to keep it in solution and diluted to 1000 ml. in a graduated flask. One hundred ml. of this solution is diluted to 1000 ml. One ml. of this diluted solution contains 0.0001 gram bismuth.

Procedure. ***Isolation of Bismuth.***—The solution is freed from lead by H_2SO_4, and from arsenic, antimony, and tin by precipitation of the sulfides and extraction with Na_2S solution. The residual sulfides are dissolved in hot dilute nitric acid, according to the standard methods of procedure. The free nitric acid is nearly neutralized by the cautious addition of dilute ammonia, the last portion being added drop by drop, until a faint cloudiness is evident, and then 10 to 15 ml. of 10% ammonium carbonate are added with constant stirring. The mixture is digested for about three hours on the steam bath, the clear solution decanted through a small filter, the residue washed by *decantation once or twice with hot water containing ammonium carbonate and then on the filter twice with pure hot water.*

Colorimetric Comparison

The residue of bismuth basic carbonate is dissolved in the least amount of dilute nitric acid necessary to effect solution and the filter washed free of bismuth with a little water containing a few drops of nitric acid. The solution is made up to a definite volume, 50 ml. or 100 ml. according to the bulk of precipitate dissolved. Two small beakers placed side by side may be used for the color comparison, a sheet of white paper or tile being placed under the beakers. Two 50-ml. Nessler tubes, however, are preferred. Three ml. of cinchonine solution are added to each container. From a burette the bismuth nitrate sample is run into one of these containers in just sufficient quantity to

[12] Method of W. C. Ferguson.

color the reagent a crimson or orange tint. The exact volume required to do this is noted and the equivalent amount of sample used calculated. (If no color is produced bismuth is absent.) The reagent in the adjacent beaker or Nessler tube is diluted to 5 to 7 ml., and into this is run, from a burette, the standard bismuth nitrate solution until the color exactly matches the sample. From the ml. of the standard required the amount of bismuth in the sample can readily be calculated.

Reaction.—$3KI + C_{19}H_{22}N_2OKI + Bi(NO_3)_3 = C_{19}H_{22}N_2OKIBiI_3 + 3KNO_3$.

Precautions.—The sensitiveness of the method is lost if the depth of color is too great. It is necessary, then, to add the sample to the cinchonine reagent in such quantity only as will produce a light crimson or orange color.

Solutions in the comparison tubes or beakers must not be overdiluted, since the bismuth salt formed by the reaction of the cinchonine reagent is soluble in water with the disappearance of color in too dilute solutions.

Comparison must be expeditiously made, as a precipitate is apt to form upon standing, and iodine will sometimes separate.

The order of addition must be observed; e.g., the bismuth solution is added to the cinchonine reagent, never the reverse.

COLORIMETRIC DETERMINATION OF BISMUTH. BISMUTH IODIDE METHOD[13]

Bismuth iodide gives an intense yellow, orange, or red color to its solution. The color is not destroyed by SO_2, as is that of free iodine. The intensity of the color varies as follows:

1 part of bismuth in 10,000 parts of water produces an orange-colored solution.
1 part of bismuth in 40,000 parts of water produces a light orange color.
1 part of bismuth in 100,000 parts of water produces a faint yellow color.

Reagents. ***Standard Bismuth Solution.***—One gram of bismuth is dissolved in 3 ml. of conc. nitric acid and with 2.8 ml. of water and made up to 100 ml. with glycerine. Glycerine is added to keep the BiI_3 in solution. Glycerine is not necessary for amounts of bismuth below 0.0075 gram per ml.

Potassium Iodide Solution.—Five grams of potassium iodide dissolved in 5 ml. of water is diluted to 100 ml. with glycerine.

Procedure.—The sample is dissolved with just sufficient nitric acid and *water necessary to cause solution, 10 ml. of glycerine and 10 ml. of potassium iodide solution added and the sample diluted to 50 ml.* Comparison is now made with 10 ml. of the standard bismuth solution to which has been added 10 ml. of potassium iodide and 30 ml. of water. It is advisable to have the standard stronger in bismuth than the sample and to draw out the standard from the comparison cylinder until the two colors match.

BISMUTH DETERMINATION IN LEAD BULLION[14]

Ten to twenty-five grams of the lead, hammered or rolled out and cut into small pieces, are taken for analysis. The sample is dissolved in a mixture of 200 ml. water and 50 ml. nitric acid (sp.gr. 1.4) in a large covered beaker, and warmed gently on water or steam bath. When lead has dissolved, the beaker

[13] T. C. Thresh, Pharm. Jour., 641, 1880. Copper and ferric iron interfere.
[14] J. J. Mulligan.

is removed and placed on cool surface and enough sulfuric acid (1–1) added to precipitate lead.

The lead sulfate is allowed to settle and the clear supernatant liquid is decanted into another beaker and held. To the residue of lead sulfate 10–20 ml. concentrated sulfuric acid is added and brought down to strong fumes on hot plate. After strong fuming, the portion containing lead sulfate is diluted with water. To the first clear decanted portion, 10 ml. sulfuric acid is added and this also evaporated down to fumes of sulfuric acid. Both portions are removed from hot plate and when cool add 50 ml. water and 3 to 5 grams of tartaric acid to each. Heat to dissolve tartaric acid and filter over asbestos pad, the clear portion first, and then follow with the one containing bulk of lead sulfate. The bulk of lead sulfate is washed by decantation three or four times with warm water before transferring to asbestos pad. When bismuth is higher than .30% in the bullion, the sulfate residue may be retreated with sulfuric acid, fumed and washed. The clear solution is allowed to stand for one hour and refiltered to ensure removal of all lead sulfate. The filtrate is then warmed and hydrogen sulfide gas passed; filtered on a paper and washed with cold H_2S water. The sulfides are washed from filter back to precipitating beaker. The sulfides of Sb, Sn, Te, etc., are leached out with a 10% K_2S solution, which has been saturated with hydrogen sulfide, and allowed to stand in warm place and filtered over the original sulfide paper. After washing with warm water containing a few drops of K_2S solution, the precipitate is dissolved in nitric acid and a few drops of bromine to ensure solution of all sulfur. It is all important to remove Sb, Sn and Te from sulfide precipitate before going any further by repeating hydrogen sulfide precipitation.

The nitric acid solution of Bi, Cu, etc. is made faintly alkaline with ammonia and 1 gram ammonium carbonate added and the solution boiled for five to ten minutes when the bismuth is precipitated as basic salt. To ensure solution of the copper, a few drops of free ammonia are added with stirring before filtering. The bismuth precipitate is filtered on a tared Gooch, washed with water, dried and ignited to Bi_2O_3 over Bunsen flame.

$$Bi_2O_3 \times .8970 = Bi.$$

If the bismuth precipitate is dark after precipitation with ammonia and ammonium carbonate, it may be due to tellurium. If so, the filtered precipitate is dried, ignited and fused with caustic potash and sulfur to put the tellurium in a soluble form and thus remove tellurium from insoluble bismuth sulfide; or redissolving in acid and reprecipitating as sulfides and washing the sulfides with K_2S solution as before mentioned.

This method is applicable to refined lead when larger portions are taken.

BISMUTH IN ALLOYS[15]

The alloy is dissolved in nitric acid, as little hydrochloric as possible, and 10 ml. sulfuric, and run down to strong SO_3 fumes. Then proceed as for ores.

[15] A portion of this chapter was contributed by J. J. Mulligan, Superintendent, U. S. S. Lead Refinery, Inc.

Where bismuth is present with considerable tin, the cementation of the bismuth with pure iron wire to free it from tin and then treatment of the residue as for ores and mattes, seems to be the best means for obtaining a bismuth preparation free of tin for control analyses.

In the presence of considerable copper, the bismuth can be precipitated as basic carbonate, filtered, and the impure basic precipitate treated with nitric acid and evaporated to fumes of sulfuric, the procedure then being the same as for ores and matte.

DETERMINATION OF BISMUTH IN ORES, MATTES

A qualitative test for lead and insoluble bismuth compounds on all products to be analyzed for bismuth is an important step with the removal of lead as sulfate as soon as perfect solution of the sample is insured.

For products containing from $\frac{1}{2}$% to 25% bismuth, one gram portions are taken; for 50% or higher $\frac{1}{2}$ gram portions are weighed up.

The weighed portion is transferred to a 250-ml. beaker and 25 ml. H_2O and 10 ml. concentrated nitric acid added, and where sulfur is present a few drops of bromine are added cautiously after acid has been allowed to act for a sufficient time. After all sulfur has gone in solution, boil down to dryness on water bath or hot plate, 2 ml. of nitric acid and 1 ml. hydrochloric acid are added, then 10 ml. of sulfuric acid cautiously added, and the covered sample taken down on hot plate to strong fumes of SO_3. The cooled solution is diluted with 50 ml. water and 2 to 3 grams tartaric acid are added and the mixture brought to a boil. The residue containing insoluble lead sulfate, silica and other insolubles is filtered and washed with 2% solution of sulfuric acid to free residue of soluble bismuth.

The filtrate contains Bi, Cu, Sb, As, Te, and a small amount of Pb may be in the solution. After standing for one-half hour or more, the solution is refiltered to remove any lead that may have gone through on first filtration.

The clear solution containing bismuth is saturated with hydrogen sulfide gas for one-half hour.

Filter sulfides on filter paper and wash with H_2S water. If much iron is present the sulfides are redissolved in nitric and sulfuric acids, taken to fumes, and the sulfide precipitation repeated.

The sulfides are leached with a 10% solution of K_2S saturated with H_2S gas to remove As, Sb, Sn, Te and Se. The remaining sulfides containing Cu, Cd, Bi are dissolved in nitric acid and a little bromine water, bromine boiled off and solution made slightly alkaline with ammonia water and 1 gram of ammonium carbonate added. The solution is boiled for five to ten minutes and 1 ml. of ammonia is added and the basic carbonate filtered on a tared Gooch, ignited and weighed as Bi_2O_3.

$$Bi_2O_3 \times .8970 = Bi.$$

BORON

B, *at.wt.* 10.82; $\begin{cases} \textit{amorp. sp.gr. } 2.45; \textit{ m.p. } 2200°; \textit{ b.p. sublimes.} \\ \textit{cryst. sp.gr. } 2.55; \textit{ m.p. } 2500°; \textit{ b.p. } 3500° \text{ C.}; \textit{ oxide}, B_2O_3 \end{cases}$

Boron occurs combined in nature as boric acid, and the combination of this acid with certain bases. It is frequently associated with calcium and aluminum in siliceous rocks in such minerals as datolite, a calcium boro-silicate; axinite, a calcium aluminum boro-silicate; tourmaline, a complex boro-silicate. The commercial sources of boron are borax, $Na_2B_4O_7 \cdot 10H_2O$ (36.6% B_2O_3); tincalconite (tincal) ($Na_2O \cdot 2B_2O_3 \cdot 5H_2O$) found in great quantities in the Mojave desert in southern California; kernite, $Na_2B_4O_7 \cdot 4H_2O$; ulexite, $NaCaB_5O_9 \cdot 8H_2O$ (43% B_2O_3); colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$ (50.9% B_2O_3); boracite, $Mg_7Cl_2B_{16}O_{30}$ (62.5% B_2O_3) and kramerite ($Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 10H_2O$) (49.5% B_2O_3). The demand for boron in the past twenty years has increased three fold.

DETECTION

Flame Test.—Boric acid is displaced from its salts by nearly all acids, including even carbonic acid. Upon ignition, however, it in turn drives out other acids which are volatile at lower temperatures. A powdered borate, mixed with potassium sulfate and calcium fluoride, placed on the loop of a platinum wire, is held in the colorless flame of a Bunsen burner, a green color will be imparted to the flame by boron. Copper salts should be removed with H_2S and barium as $BaSO_4$ if present, as these also color the flame green.

The flame test may be conveniently made by treating the powdered sample in a test-tube with sulfuric acid and alcohol (preferably methyl alcohol). A cork carrying a glass tube is inserted and the test-tube gently warmed. The escaping gas will burn with a green flame.

The test may be made by igniting the mixture of powder, alcohol, and sulfuric acid in an open porcelain dish. The green color will be seen in presence of a borate. The test is not as delicate as the one with the test-tube.

Borax Bead.—$Na_2B_4O_7 \cdot 10H_2O$ fused in a platinum loop, swells to several times its original volume as the water of crystallization is being driven out, then contracts to a clear molten bead. If the bead is dipped into a weak solution of cobalt and plunged into the flame, until it again becomes molten, the bead upon cooling will be colored blue.

Turmeric Test.—A few drops of acetic acid are added together with 2 or 3 drops of an alcoholic turmeric solution to an alcoholic extract of the sample, placed in a porcelain dish. The solution is diluted with water and then evaporated to dryness on the water bath. 1/1000 milligram of boric acid will produce a distinct color, 2/100 milligram will give a strong reddish-brown colored residue, which becomes bluish-black when treated with a drop of sodium hydroxide solution.[1]

Boron was isolated by Gay-Lussac and L. Thenard (1808) by reduction of the trioxide with potassium. Sir Humphrey Davy obtained it about the same time by reduction of boric acid.

Borax is an important constituent of enamels. It is employed in glass, which is used for making chimneys and incandescent lights and other heat resisting glassware. It is used to protect the citrous fruit from "blue mold." Compounds of boron have a marked effect on plant growth.

ESTIMATION

The determination of boron (generally reported as B_2O_3) may be required in a variety of substances, boron bearing ores, borax, alkaline brines, soils, commercial boric acid and borate concentrates, ceramic materials, paint pigments, food preservatives etc.

During an analysis boron may be left in part with the silica residue causing high results for silica, as it volatilizes with silicon tetrafluoride during the treatment of SiO_2 with HF and H_2SO_4. A portion may be carried down with the ammonium hydroxide precipitate giving high results for aluminum.

In the decomposition of the substance for the determination of boron care must be exercised to avoid the loss of boron, as boric acid is easily liberated from its combinations by acids and volatilizes with steam. Digestions carried out in covered beakers practically eliminates the loss provided the heating is done cautiously avoiding vigorous boiling. Loss occurs if the digestion is conducted in uncovered beakers.

The reagents used in the determination should be free from boron as well as the glass vessels in which the reactions are conducted.

PREPARATION AND SOLUTION OF THE SAMPLE

Crystalline boron is scarcely attacked by acids or alkaline solutions; the amorphous form, however, is soluble in concentrated nitric and sulfuric acids. Both forms fused with potassium hydroxide are converted to potassium meta-

[1] Turmeric test—G. Bertrand and H. Agulhon, Compt. rend., **157**, 1433, 1913.

borate. Boric acid is more readily soluble in pure water than in hydrochloric, nitric, sulfuric or acetic acids, but is more soluble in tartaric acid. Borax is insoluble in alcohol. The addition of an acid to borax liberates boric acid, forming at the same time the salt of the added acid.

Boronatrocalcite, Ulexite, Colemanite, Water-Insoluble Borates.—A five to ten gram sample of the material is digested in a flask with reflux condenser with sufficient hydrochloric acid to combine with the bases with which boric acid is united. Following the digestion (an half hour is generally sufficient) the sample is filtered, and the filtrate and washings of the residue and apparatus transferred to a volumetric flask and diluted to definite volume. If preferred the material may be transferred to a volumetric flask, made to volume and allowed to settle, and aliquot portions filtered for analysis, using dry filters. Allowance is made for the residue in the flask.

Borax, Borax Concentrates, Tincal, Rasorite, Water-Soluble Borates.—Details for evaluation will be found in a later section of this chapter.

Boric Acid in Mineral Water.—Water containing more than 0.1 gram boric acid per liter, about 200 ml. are evaporated to small volume, the precipitated salts are filtered off and washed. Boric acid passes into the filtrate and may be determined by the distillation method of Gooch given on p. 166.

With water containing traces of boric acid, 5 liters or more are evaporated to about one-tenth the original volume the precipitate filtered off and washed with hot water. The filtrate is evaporated down to a moist residue. If the residue is small, it is acidified with acetic acid and the boric acid determined by distillation, as stated on p. 166. If considerable residue is present, hydrochloric acid is added to acid reaction, and then the mixture digested with absolute alcohol in a corked flask for ten to fifteen hours, with occasional shaking. The solution is filtered, the residue washed with 95% alcohol, the filtrate diluted with water, 10 ml. of 10% sodium hydroxide solution added and the alcohol distilled off. A second alcoholic extraction is generally recommended. The final alkaline solution is taken to dryness and gently ignited. The residue is extracted with water, made acid with acetic acid and B_2O_3 determined by distillation.

Carbonates.—The material is treated with sufficient acid (M. O. indicator) to liberate all the CO_2 and react with the combined alkali of boric and carbonic acid; it is boiled in a flask with reflux condenser to expel CO_2, ten to fifteen minutes, the solution exactly neutralized with sodium hydroxide (M. O.), and the liberated boric acid titrated in presence of glycerol and phenolphthalein as usual.

If cautiously conducted the expulsion of CO_2 may be effected in a covered beaker without loss of boric acid.

Boric Oxide in Silicates, Enamel, etc.—About 0.5 gram of the finely ground material is fused with five times its weight of sodium carbonate, the melt extracted with water and the extracts, containing the sodium salt of boric acid, evaporated to small volume. The greater part of the excess sodium carbonate is neutralized with hydrochloric acid and finally made acid with acetic acid (litmus paper test=red). Boric oxide is now determined by the distillation process according to the procedure given later in the chapter.

Acid Insoluble Boron Minerals.—Minerals in which boron is not completely liberated by acid treatment must be fused with sodium carbonate in a platinum crucible, the flux being weighed. The fusion is dissolved by adding the

necessary amount of standard acid to neutralize the base and then a slight excess. During the neutralization heating is avoided. Should the volumetric titration method be followed in the subsequent analysis it is necessary to expel the carbon dioxide in solution, but considerable care should be exercised to avoid loss of boric acid, which is volatile with steam. A reflux condenser will prevent loss, if boiling the solution is necessary to effect expulsion of CO_2, or the expulsion may be accomplished in a covered beaker, heating at "simmering" temperature for 10–15 minutes.

Boron Carbide.—See p. 181.

SEPARATIONS

Boron may be separated from other interfering elements by distillation in presence of acid and methyl alcohol according to the procedure given under the methods that follow. See Distillation Method as modified by Chapin.

Boric Acid in Milk, Butter, Meat and Other Foods

Milk.[2]—One hundred ml. of milk is treated with 1 to 2 grams of sodium hydroxide, and evaporated to dryness in a platinum dish. The residue is thoroughly charred[3] by gently heating; at this stage care must be exercised or loss of boric acid will result; 20 ml. of water are added, the sample heated and hydrochloric acid added drop by drop until all but the carbon has dissolved. The mixture is washed into a 100-ml. flask with as little water as possible, 0.5 gram calcium chloride added, then a few drops of phenolphthalein indicator, then a 10% sodium hydroxide solution until a slight permanent pink color is obtained and finally 25 ml. of lime water. (All P_2O_5 is precipitated as calcium phosphate.) The liquid is made to 100 ml., mixed thoroughly, and then filtered through a dry filter. To 50 ml. of the filtrate, equivalent to 50 ml. of the milk taken, normal sulfuric acid is added until the pink color disappears, then methyl orange indicator is added, followed by more of the standard acid until the yellow color changes to a faint pink. Carbon dioxide is expelled and the liberated boric acid titrated in presence of glycerine, according to the procedure given for evaluation of borax and boric acid, under "Volumetric Determination of Boron."

Butter.[4]—Twenty-five grams of butter are weighed out in a beaker and 25 ml. of a sugar sulfuric acid mixture added. (Mix = 6 grams sugar of milk, 4 ml. normal sulfuric acid per 100 ml. of solution.) The beaker is placed in the oven (100° C.) until the fat is melted and the mixture is thoroughly stirred. When the aqueous solution has settled, 20 ml. are pipetted out, phenolphthalein added, the solution brought to boiling and half-normal sodium hydroxide added until a faint pink color is obtained. Ten ml. of neutral glycerine are added and the titration carried on until a permanent pink color appears. The difference between the two titrations multiplied by the factor for equivalent boric acid gives the weight of boric acid in the portion taken.

The determination is not affected by the phosphoric or butyric acid or by the sugar of milk in the butter.

[2] R. T. Thomson, Glasgow City Anal. Soc. Repts., 1895, p. 3.
[3] The milk residue thoroughly charred will give a colorless solution upon extraction.
[4] H. Droop Richmond and J. B. P. Harrison, Analyst, 27, 197.

Meat.[5]—Ten grams of the chopped meat are mixed in a mortar with 40 to 80 grams of anhydrous sodium sulfate, and dried in the water oven. The mass is powdered, then placed in a flask and 100 ml. of methyl alcohol added and allowed to stand for about twelve hours. The alcohol is distilled into a flask and saved. Fifty ml. more of alcohol are added to the residue and this again distilled into the first distillate. The distillates are made up to 150 ml., a 50-ml. portion diluted with 50 ml. of water and 50 ml. of neutral glycerine added with phenolphthalein indicator, and the boric acid titrated with twentieth-normal sodium hydroxide.

$$\text{One ml. N/20 NaOH} = 0.003092 \text{ gram boric acid, } H_3BO_3.$$

Boric acid in canned goods, sauces, cereals, etc., may be determined by evaporation of the substance with sodium hydroxide and incineration as in case of milk. The sodium hydroxide is neutralized and boric acid titrated as usual.

GRAVIMETRIC DETERMINATION OF BORON

The solubility of boron compounds prevents complete precipitation by any of the known reagents, hence most of the gravimetric methods are indirect.

DISTILLATION AS METHYL BORATE AND FIXATION BY LIME[6]

This excellent method, originally worked out by F. A. Gooch,[6] and later modified by Gooch and Jones,[7] depends upon the fact that the borates of alkaline earths and alkalies give up their boron in the form of the volatile methyl borate (*b.p.*, 65° C.), when they are distilled with absolute methyl alcohol (acetone-free). The methyl borate passed over lime in presence of water is completely saponified, the liberated boric acid combining with the lime to form calcium borate, which may be dried, ignited, and weighed. The increase of the weight of the lime represents the B_2O_3 in the sample.

$$2B(OCH_3)_3 + CaO + 6H_2O = 6CH_3OH + Ca(BO_2)_2 + 3H_2O.$$

Procedure.—About 1 gram of pure calcium oxide is ignited to constant weight over a blast lamp and then transferred to the dry, Erlenmeyer receiving flask (Fig. 17). The crucible in which the lime was heated and weighed is set aside in a desiccator for later use.

[5] C. Fresenius and G. Popp, Chem. Centr., 2, 69, 1897.
[6] Proc. Am. Acad. of Arts and Sciences, 22, 167–176, 1886. Anal. Chem., Treadwell-Hall, Vol. 2.
[7] See note on p. 168.

0.2 gram or less of the alkali borates, obtained in solution by a procedure given under "Preparation of the Sample," is treated with a few drops of litmus (or lacmoid), solution and the free alkali neutralized with dilute HCl solution added drop by drop. A drop of dilute sodium hydroxide solution is added and then a few drops of acetic acid. The slightly acid solution is transferred to the pipette-shaped retort *R*, Fig. 17, by means of the attached funnel *F*, washing out the beaker and funnel with three 2- to 3-ml. portions of water. The stopcock of the funnel is closed, the apparatus is connected up as shown in the illustration, the paraffin bath, heated to not over 140° C., placed in position [8] and the liquid in the retort distilled into the receiver containing the known amount of lime. When all the liquid has distilled over, the paraffin bath is lowered, the retort allowed to cool for a few minutes, 10 ml. of methyl alcohol (acetone-free) added to the residue in *R* and the contents again distilled by replacing the paraffin bath. The process is repeated three times with methyl alcohol. The contents of the retort (which are now alkaline), are made distinctly acid by addition of acetic acid, and three more distillations made with 100-ml. portions of methyl alcohol, as before. The paraffin bath is now removed, the receiving flask is stoppered, the contents thoroughly mixed by shaking, and set aside for an hour or more for complete saponification of the methyl borate. The contents are now poured into a large platinum dish and evaporated on the water bath at a temperature below the boiling-point of the alcohol. (Loss of boric acid will occur if the alcohol boils.) The adhering lime in the receiving flask is dissolved by wetting its entire surface with a few drops of dilute nitric acid (the flask being inclined and revolved to flow the acid over its sides). The contents are transferred to the dish with a little water and the evaporation repeated. No loss of boric acid will take place at this stage, the alcohol having been removed during the first evaporation. The residue is gently heated to destroy any calcium acetate that may have formed, the cooled borate and lime are taken up with a little water and transferred to the crucible in which the lime was heated and weighed. The material clinging to the dish is dissolved with a little nitric acid (or acetic acid), and washed into the crucible. The contents of the crucible are evaporated to dryness on the water bath, then heated very gently over a flame (the crucible being covered) and finally more strongly. The heating is continued until a constant weight is obtained. The increase of weight of the lime represents the amount of B_2O_3 in the sample.

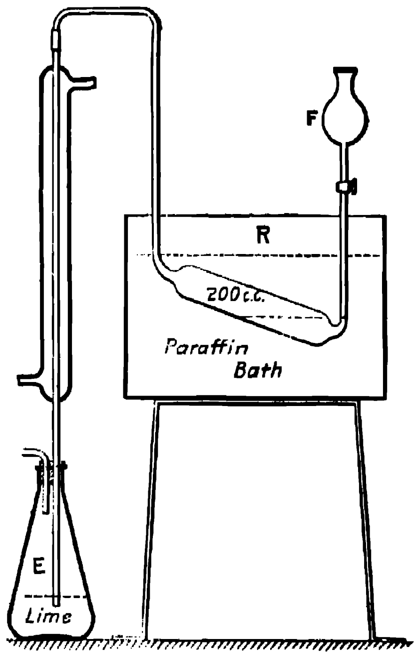


Fig. 17.—Distillation of Methyl Borate.

[8] Submerge the retort in the paraffin bath gradually to prevent too violent a reaction.

NOTES.—Gooch and Jones worked out a procedure which utilizes sodium tungstate as a retainer of the methyl borate, in place of the lime. This substance is definite in weight, not hydroscopic, soluble in water, and recoverable in its original weight after evaporation and ignition. "Methods in Chem. Anal.," p. 204, 1st Ed. By F. A. Gooch, John Wiley & Sons, Publishers.

The receiving flask has a cork stopper with a hole to accommodate the tube of the condenser and a slit to permit the escape of air from the flask.

Gooch recommends cooling of the receiving flask.

VOLUMETRIC DETERMINATION OF BORON

Introductory.—The boron bearing material is brought into solution by an appropriate method and the solution freed from carbon dioxide, aluminum, iron and any substance other than boric acid which reacts with sodium hydroxide. If the solution is alkaline it is made slightly acid and heated to expel carbon dioxide (covered beaker). Boric acid is liberated by the acid treatment. The free mineral acid is very carefully neutralized in presence of a suitable indicator, which is unaffected by free boric acid, such as methyl orange, methyl red, or Sofnol Red No. 1. With the indicators mentioned the end-point is the first definite yellow color. A polyhydric alcohol is added (mannitol or glycerol are generally used, glucose has been found to be satisfactory) and the titration of boric acid by means of standard alkali, is conducted in presence of a suitable indicator, such as phenolphthalein. In the presence of glycerol the following reaction has been suggested:

$$C_2H_5OH\cdot HBO_3+NaOH=C_3H_5OH\cdot NaBO_3+H_2O.$$

1 ml. of 1 N NaOH is equivalent to 0.03482 g. B_2O_3.

Removal of Carbon Dioxide.—This is accomplished by slightly acidifying the solution and heating gently for ten to fifteen minutes in a covered beaker. Vigorous boiling must be avoided as loss will occur with the resulting steam. Loss also occurs if the beaker is uncovered during the expulsion of the CO_2. If carbon dioxide is not completely expelled the results will be too high for boric acid.

Removal of Iron and Aluminum.—The precipitation of the hydroxides of these elements by addition of an alkali hydroxide to the ferric or aluminum salts would lead to high results for boric acid, hence iron and aluminum should be removed from the solution titrated. Various methods have been suggested for the removal of iron and aluminum, by precipitation with magnesium oxide or by addition of barium or sodium carbonates, or sodium hydroxide in presence of boric acid with a suitable indicator which would avoid an excess of the alkali (aluminate will form with an excess). Since the hydroxides occlude boric acid, provision is made for determining the occluded acid. Ammonium hydrox-

ide should not be used for precipitation of iron and aluminum as it leads to high results for boric acid, the ammonium chloride formed reacting with the alkali hydroxide. Details of analysis for the commercial evaluation of borates follow.

EVALUATION OF CRUDE BORATES

The procedures below are applicable for the determination of water soluble and total borates in borax, kernite, tincalconite, ulexite, colemanite, boracite etc. Should boro-silicates be present, conversion to the soluble sodium salt may be effected by fusion with sodium carbonate. It is very necessary that the analysis be conducted on representative samples. Borate concentrates rapidly pick up moisture so that the samples must be kept sealed from the air to obtain concordant results.

DETERMINATION OF WATER SOLUBLE BORATES

Crude borates generally contain shale, which must be separated from the water soluble borates. This is accomplished by extraction with sufficient water to dissolve the soluble borates; which, in crude borax, tincalconite, kernite and other sodium borates, constitute practically all of the available borates. In presence of iron and aluminum, which is left entirely with the residue from the water extraction, some boric acid invariably is occluded in the residue and must be recovered, should total boric acid be desired. Details for the estimation of borate in the residue are given.

Reagents.—Normal or half normal hydrochloric acid. Normal or half normal sodium hydroxide (CO_2 free). Approximately sixth normal hydrochloric acid. Mannitol or glycerol (neutral). Indicators. Carbonate free water.

Preparation and Extraction of the Sample

A five gram sample is taken from the representative, finely ground material and is placed in a 250-ml.–300-ml. beaker, 200 ml. of pure water are added, the beaker covered and placed on a hot plate and brought to gentle simmering. After 15–20 minutes of heating, with occasional stirring, 2–3 ml. of sodium chloride crystals are added and the residue allowed to settle clear (10–15 minutes of settling is generally sufficient). The clear solution is carefully decanted through a rapid filter into a 500-ml. graduated flask, taking care to avoid transferring any residue to the filter as this would seriously retard filtration. The extraction of the residue is repeated three times more with 75 ml. portions of pure water, settling each time with addition of 1 ml. of solid sodium chloride crystals, and cautiously decanting the solution through the

filter into the flask. The extractions are best made by gently heating, and stirring, for a few minutes with each 75 ml. portion. Practically all of the soluble borates are extracted with the first two portions. Finally the residue is transferred to the filter by a 1% solution of NaCl and the filter allowed to drain. If much shale is present with iron and aluminum hydroxides this last step is slow. (If the residue is not to be examined for occluded and insoluble borates, the procedure may be greatly hastened by transferring the extracts and the final residue directly to the flask without filtration. An allowance of 0.5 ml. for the residue is generally more than sufficient for the space occupied by this.) The 500-ml. flask is now filled to the mark with distilled water and thoroughly mixed. Aliquot portions are taken for analysis, usually 100 ml. (1 g.) when half normal reagents are to be used, or 200 ml. (2 g.) when normal reagents are used.

Titration of Boric Acid.—To the solution in a 250-ml. beaker are added 2–3 drops of Sofnol Red No. 1, methyl red, or methyl orange indicator and just sufficient 6 N HCl to give a red color and about 0.3–0.5 ml. excess. The beaker is covered and the solution gently heated to simmering temperature, avoiding vigorous boiling. Ten minutes is sufficient to expel carbon dioxide. (CO_2 if present would cause high results.) The solution is cooled by placing the beaker in a container of cold water. The solution and cover rinsings are carefully neutralized by addition of just sufficient standard alkali to give a yellow color. (A drop of the reagent will give this color at the end-point.) The free boric acid is now titrated, after the addition of 25–50 ml. of glycerol (or 4–8 grams of mannitol) and 1 ml. of phenolphthalein indicator. The standard alkali is added until a faint pink color is obtained, and then a drop or more additional, until the color is a definite reddish pink, the true end-point.

1 ml. 1 N NaOH is equivalent to 0.03482 g. B_2O_3.

1 ml. 0.5 N NaOH is equivalent to 0.01741 g. B_2O_3.

Determination of Boric Acid in the Water Insoluble Residue

The residue on the filter from the water extraction is washed into a tall 250-ml. beaker, 10 ml. of 6 N HCl added, the beaker covered and the mixture heated gently on a hot plate, just below boiling, for 15–20 minutes. (No loss of boric acid results under these conditions. With vigorous boiling a loss will occur.) The solution is cooled, filtered, and powdered sodium carbonate added to the filtrate until the free HCl is neutralized (avoiding an appreciable excess), the solution reacting blue to litmus paper. The iron, aluminum, and silica are filtered off. Boric acid is determined in the filtrate and washings of the residue, according to the procedure for titration of boric acid, as described:—acidification with acid, expulsion of CO_2, neutralization to Sofnol Red or methyl orange as indicator, and titration of boric acid in presence of glycerol and phenolphthalein.

Notes.—If much residue is present a second treatment may be necessary. If silico-borates are present the residue should be fused with sodium carbonate and the borate determined in the fusion.

A 5 gram sample is ample, larger amounts are difficult to handle and are unnecessary.

The finely divided clay remains in suspension for hours and would be difficult to filter. The addition of sodium chloride flocculates this suspended matter, causing it to settle rapidly. The added salt does not affect results.

It is important to wash by decantation, otherwise the finely divided clay will clog the filter and greatly lengthen the time of filtration and washing.

Carbonates must be expelled from the solution that is titrated for boric acid, as CO_2 leads to high results. In covered beakers no loss of boric acid occurs during this expulsion of CO_2. By experiment it was found that at simmering temperature no loss occurred during 45 minutes of heating in a covered beaker, while there was a loss of 8.7 milligrams from a total of 491 milligrams during the same period of time in an uncovered beaker.

Glycerol is apt to contain free fatty acids. Should these be present, prepare the glycerol as follows:—To a liter of glycerol add 100 ml. of distilled water and 10 ml. of phenolphthalein indicator. Now cautiously add standard sodium hydroxide until a faint pink color is obtained.

Where doubt exists regarding the end-point in the boric acid titration, add 6 N HCl until the red color of methyl orange or methyl red is obtained. Neutralize with NaOH and repeat the titration of boric acid with NaOH.

The reagents should be carbonate free.

All analysis should be conducted on the sample that is representative. The calcined borate concentrate rapidly picks up moisture so that the sample should be kept in an air tight container.

Iron and aluminum carry out boric acid in direct proportion to the amount of these hydroxides present. Recovery of the occluded or adsorbed boric acid must be accomplished if total boric acid is desired. A double precipitation is seldom necessary of the iron and aluminum from which a recovery is made, since the amount generally present in the reprecipitation is inappreciable, unless the precipitate is large.

Precipitation of iron and aluminum by addition of ammonium hydroxide has been suggested. This is highly undesirable as the presence of ammonium salts lead to a serious error in the titration of boric acid and the end-point is uncertain. Ammonium salts are difficult to expel from the solution.

EVALUATION OF BORON BEARING ORES—ACID EXTRACTION METHOD

The method is applicable for the determination of total boric acid in borates of sodium, calcium, and magnesium in materials such as crude borax, tincalconite, kernite, boracite, ulexite, colemanite etc. Silicoborates require a preliminary fusion with sodium carbonate. The acid residue should be examined for these. Iron and aluminum, ammonium salts and substances other than boric acid, should be absent from the solution if they react with sodium hydroxide.

Reagents.—1 N or 0.5 N HCl and NaOH (carbonate free). 6 N HCl (acid of constant boiling point is satisfactory). Saturated solution of sodium hydroxide (carbonate free). Water (carbon dioxide free). Indicators—Sofnol Red No. 1. Para-nitro-phenol saturated water solution; Phenolphthalein 1.0% in a 50% alcohol solution. Mannitol or Glycerol.

Procedure Acid Extraction.—A five gram sample, finely ground, is placed in a 250-ml. volumetric flask, 15–20 ml. of 6 N HCl are added, together with an

equal volume of water and the flask connected to a reflex condenser. The mixture is heated to boiling and boiled for 20–25 minutes. After allowing to cool slightly, 75 ml. of water are poured into the flask through the condenser tube, the solution mixed, and then the heating and boiling repeated for 10–15 minutes. The flask is again allowed to cool slightly and about 50 ml. of water poured through the condenser tube into the flask. The condenser is disconnected, the flask placed in a cold water bath and cooled. Water is now added to the 250 ml. mark, and if necessary an additional amount to allow for the volume occupied by the residue. One gram of the residue occupies a volume slightly less than 0.5 ml. Generally the amount is so small that this additional water is unnecessary. After the residue has settled, the clear solution, in the quantity desired, is decanted through a dry filter into a dry, clean beaker, and portions of this filtrate taken for analysis. Fifty ml. are equivalent to 1 gram of the original sample.

Volumetric Determination of Boric Acid.—Fifty ml. of the filtrate or 100 ml. are taken, according to the strength of the reagents used. The work is conveniently carried out in 400-ml. beakers.

Removal of Iron and Aluminum.—Salts of iron and aluminum react quantitatively with sodium hydroxide when the solutions of the compounds are combined. Iron is completely precipitated as hydroxide when its combined acid is neutralized by the NaOH, and an excess of the alkali has no further action except to make it more flocculent. Aluminum is precipitated at a pH of 6 to 7.5, but an excess of the alkali forms the soluble sodium aluminate, causing the aluminum compound to redissolve. Aluminum may be quantitatively precipitated by sodium hydroxide in boric acid solutions, in the absence of polyhydric alcohols, when using p-Nitrophenol indicator which gives a yellow color at the proper pH for the precipitation of the aluminum. The indicator shows the end-point when all of the combined acid of iron and aluminum are neutralized. Advantage is taken of this action in the removal of iron and aluminum from boric acid solutions. This avoids the introduction of an ammonium salt, which would interfere in the boric acid determination if ammonium hydroxide were used to precipitate aluminum and iron. It avoids introduction of a carbonate. When sodium carbonate is employed in this precipitation, the carbonate interferes with the boric acid titration, and must be removed by boiling the solution, slightly acidified, keeping the beaker covered, otherwise loss of boric acid occurs.

Procedure.—To the boric acid solution in a beaker are added 3–4 drops of Sofnol Red, or p-Nitrophenol indicator. Standard sodium hydroxide is added cautiously until the yellow color of the indicator remains. All the iron and the aluminum will be precipitated at this point. The solution is heated gently, then allowed to stand for several minutes. The iron and aluminum hydroxide is filtered off and washed with hot water, and the filtrate and washings titrated for boric acid according to the procedure given under titration of boric acid.

Recovery of Occluded Boric Acid.—The iron and aluminum hydroxide carry out very appreciable quantities of boric acid, when precipitated in the presence of a large excess of this acid. If the amount of these hydroxides is appreciable, the recovery of boric acid is essential for accurate results. The hydroxides are dissolved in the filter by addition of 6 N HCl, added in sufficient excess. The acid solution is caught in a beaker together with hot washings of the filter.

Three to four drops of Sofnol Red or p-Nitrophenol are added to the solution, and sodium hydroxide (50% solution) is now added dropwise until about neutral, then 0.5 N NaOH until the yellow color of the indicator remains. The solution is gently heated and allowed to stand for several minutes and the iron and aluminum hydroxides filtered off. The filter is washed with warm water. The filtrate is now acidified with 0.5 N HCl. The solution is neutralized to Sofnol Red or p-Nitrophenol by addition of NaOH dropwise, and the boric acid determined by titration with NaOH in the presence of mannitol or glycerol (about 5 ml.) and phenolphthalein indicator. Time is saved by carrying this titration separately from the main solution.

Titration of Boric Acid.—The solution from the precipitation of iron and aluminum is acidified again with HCl and then just neutralized cautiously with NaOH to yellow color of Sofnol Red or p-Nitrophenol. Now about 10 drops of phenolphthalein indicator are added and 25–50 ml. of neutral glycerol, or solid mannitol (according to the amount of boric acid titrated) and then the standard alkali until a distinct reddish pink color appears, the true end-point for boric acid (pH 11).

NOTE.—The boric acid in the solution recovered from the iron and aluminum precipitate is determined also as directed above, and the amount added for total percentage of B_2O_3.

One ml. 1 N NaOH is equivalent to 0.03482 g. B_2O_3; or 0.09536 g. $Na_2B_4O_7 \cdot 10H_2O$; or 0.06184 g. H_3BO_3.

One ml. 0.5 N NaOH is equivalent to half the above amounts.

NOTES ON THE ACID EXTRACTION METHOD FOR TOTAL ACID

The acid extraction generally effects complete solution of the borates that are available in crude borate minerals. Should silico-borates be present a fusion of the acid residue should be made with sodium carbonate flux, and the fusion examined for borates.

The reflux condenser is used to avoid loss of the boric acid by volatilization. (The 6 N HCl is approximately acid of constant boiling point.)

The removal of iron and aluminum is necessary from the extract, as these, especially the aluminum salt, lead to high results for boric acid by the action of their combined acid with the standard base.

Definite amounts of borate are invariably carried out by the iron and aluminum hydroxides, so that a recovery must be effected if the precipitates are present in appreciable amounts.

The isoelectric point of aluminum is between pH 6–7.5, and it is at this point where the aluminum compounds are least soluble. Some aluminum hydroxide will go into solution if too much NaOH is added to precipitate the aluminum.

The end-point is a combination of the two colors yellow and pink, and is a distinct reddish pink color. The Sofnol Red or p-Nitrophenol gives a *distinct* yellow color in alkaline solutions. Both indicators are colorless in acid solutions.

A concentrated solution of NaOH is used to neutralize the 6 N HCl so as to not increase the volume for filtering.

Neutral glycerol is prepared as follows—To 1000 ml. of glycerol add 4–5 ml. of phenolphthalein and neutralize with regular NaOH reagent. The color will fade due to the formation of acid, so add more NaOH reagent as needed to keep it colored pink. A sharper end-point is obtained with mannitol.

In cases where less than .1 g. of B_2O_3 are found, greater accuracy may be obtained by use of .1 N NaOH.

If end-points are run over, back titrations are possible with either indicator.

Precipitation of iron and aluminum with NaOH in place of Na_2CO_3, avoids the necessity of expulsion of CO_2, which would cause high results for boric acid. If the latter is used, the solution should be acidified, the beaker covered and CO_2 expelled by heating gently at simmering temperature for 10–15 minutes.

It has been found, that in place of attempting to recover the boric acid in the iron and aluminum precipitate, a close result may be obtained by taking the average boric acid titrations of two equal solutions, one from which the iron and aluminum have been removed and the other in which they remain. This procedure is more rapid and will check the 3 lower methods within 0.2 to 0.3%. By actual test on a borate we obtained the B_2O_3, long method 44.04%, short method 43.87%.

Settlement Basis.—Since the borate concentrates will pick up moisture on shipment,[9] especially over seas, it is necessary that the analysis be conducted by shipper and purchaser on the same basis of moisture content. The material as shipped is spoken of as " dry " and that as received as " wet." This can be accomplished by sampling the material at the dock of shipment, and enclosing a sealed sample to the customer. Should separate samples " dry " and " wet " be examined, the settlement should be made on the average of analysis on " dry " and " wet " basis and the average of weights. For example, if 100 tons of concentrate is shipped and there is a gain of 5 tons of moisture, making a total of 105 tons received, and the analysis of the sample on the " dry " basis is 47.25% B_2O_3 and on the " wet " basis 45% B_2O_3; settlement should be made for 102.5 tons of concentrate with the average analysis of 46.12% B_2O_3.

DETERMINATION OF BORIC ACID IN CRUDE BORATES—METHOD OF THE PACIFIC COAST BORAX COMPANY [10]

In the determination of B_2O_3 in crude borates such as rasorite, colemanite, or ulexite, many elements may interfere with the direct titration. Iron, alumina, soluble silica, and manganese are common interfering substances.

To remove these substances a procedure called the " Barium Carbonate Method " is used.

The determination is based upon the fact that barium borate, formed by the addition of barium carbonate to boric acid, is quite soluble. It acts as a buffer solution of such hydrogen-ion concentration as to cause the precipitation of the hydroxides of the heavy metals. Insoluble barium compounds of the acidic compounds present such as silica, are also formed.

The method is as follows:

One gram of the finely ground borate is stirred with 50 ml. of water in a 250-ml. beaker and enough concentrated hydrochloric acid then added to

[9] By actual test on a dry concentrate a gain of over one per cent, due to moisture absorbed from the air, took place during a 2½ hour exposure of the sample to the air.

[10] Developed by G. A. Connell and K. Jacoby. Submitted by W. F. Dingley, Technical Department, Pacific Coast Borax Company.

The method in general follows the standard procedures for the determination of boric acid. Certain modifications are of interest.

decompose all the borate present. About 15 drops (1.5 ml.) are usually required. This is boiled until the borate is decomposed and dissolved, and if long boiling is found necessary it should be done under a reflux condenser. If a large excess of acid is present after the reaction is complete, it should be nearly neutralized with sodium hydroxide or sodium carbonate. Care should be taken, however, that the solution is slightly acid to methyl red before the next step is taken. A few drops of bromine water are added, enough to oxidize all the ferrous iron, and the excess of bromine boiled off. To this slightly acid solution of borate about 2 grams of finely powdered barium carbonate are added, and the solution boiled for at least two minutes. At this point the volume of the solution should be at least 100 ml. for each .5 gram B_2O_3 present, in order to avoid precipitation of B_2O_3 as barium borate. There should be a little undissolved barium carbonate left in the beaker after boiling, otherwise an insufficient quantity of barium carbonate has been used. More barium carbonate can be added at this point, if needed.

Completion of the reaction is indicated by no further evolution of carbon dioxide, and care should be taken that a sufficient application of heat has been given. After boiling, the contents of the beaker are allowed to stand for at least an hour or, if convenient, for several hours. The solution is filtered and residue washed with water. The filtrate is acidified with hydrochloric acid, boiled to remove carbon dioxide, and neutralized with N/2 sodium hydroxide solution, using methyl red as an indicator, and titrated in the same manner as given for the determination of B_2O_3 in sodium borate. When analyzing borates which have a tendency to loose moisture during preparation of the sample, or borate samples which contain associated materials which yield a precipitate difficult to filter, it is desirable to use a larger sample, say five to ten grams, conducting the preliminary treatment in a larger volumetric flask, and using an aliquot proportion for the final titration.

NOTES.—Practically all heavy metals with the exception of ferrous iron are precipitated by barium carbonate. Ferrous iron is oxidized to the ferric state and bromine water is used for this purpose, since the excess of bromine is easily removed by boiling. If excess of bromine is not removed it will decolorize the methyl red used as an indicator.

Methyl red is used as an indicator for several reasons: Its color change occurs at a hydrogen-ion concentration very close to that of boric acid solution of the strength used in the determination. Its color changes are suitable since the yellow tint does not interfere with the pink color of the phenolphthalein. Its color change is not greatly affected by temperature and fairly hot solutions may be titrated if haste is necessary. The end-points in both titrations can be sharpened by addition of 1 drop of ½% water solution of methylene blue at the time of addition of the methyl red.

When glycerine or mannitol is added to boric acid and methyl red is present, the solution will turn pink or red in color. This color should not be confused with the pink of phenolphthalein. During titration with sodium hydroxide the pink or red of methyl red will turn to yellow and remain this shade until the pink end-point of phenolphthalein is reached.

EVALUATION OF BORIC ACID

One hundred ml. of the solution, prepared as directed under " Preparation of the Sample," equivalent to 2 grams of the original material, is treated with 50 ml. of glycerol or 1 gram of mannitol, and the acid titrated with standard caustic, in presence of phenolphthalein indicator according to the procedure given under " Evaluation of Borax."

One ml. normal acid contains 0.062 gram H_3BO_3, hence the ml. of caustic required multiplied by 0.062 = grams boric acid.

Examples.—Two grams H_3BO_3 by actual test required 32.1 ml. N. NaOH $= 32.1 \times .062 = 1.99$ grams H_3BO_3.

MODIFIED CHAPIN'S DISTILLATION METHOD[11]

The method takes advantage of the volatility of methyl borate, $B(OCH_3)_3$, when alkaline earth or alkali borates are acidified, methyl alcohol added and the solution boiled. The method serves for the separation of boron from other substances and may be used as a check determination where doubt may exist regarding the accuracy of the more rapid methods described, occasioned by disagreements in evaluations of commercial boron bearing materials.

Reagents.[12]—**1. Sofnol Red No. 1 Indicator.**—0.4% in 95% ethanol, or *methyl red indicator,* 1% in 50% ethanol, is recommended[11] in place of the paranitrophenol indicator originally used in the Chapin method.

2. Phenolphthalein.—One gram dissolved in 100 ml. of ethyl alcohol and made up to 200 ml. with water.

3. Hydrochloric Acid, 0.1 Normal.—The water should be boiled to remove carbonic acid.

4. Hydrochloric Acid, 1:1 Strength.—A dropping bulb should be filled with this acid when it is needed in accurate small amounts.

5. Sodium Hydroxide, 0.5 and 0.1 Normal.—These should be standardized as follows: Fuse pure boric acid in a platinum dish. While still warm break the melt up and place the fragments quickly in a weighing tube. Dissolve 1.75 grams in 250 ml. of hot, recently boiled water, cool, and dilute the solution to 500 ml. This solution is 0.1 normal—that is, in presence of mannite or glycerol 1 ml.[13] is neutralized to the phenolphthalein end-point by 1 ml. of 0.1 normal sodium hydroxide.

In standardizing the sodium hydroxide against this solution both indicators should be used, so that the end may be the same as that seen in actual titration. Follow exactly the directions given under *b*, below, for the final titration, only assuming that the boric acid solution is exactly neutral to paranitrophenol—that is, free from mineral acid. When sodium hydroxide is standardized in this way the small amount of carbonate present does no harm.

6. Mannitol.—This is preferable to glycerol, for it requires no special preparation, does not materially increase the bulk of the solution to be titrated,

[11] " Determination of Boron in Natural Waters and Plant Materials," by L. V. Wilcox, Ind. Eng. Chem., Anal. Ed. 2, 358, Oct. 1930.

[12] Bulletin 700, " The Analysis of Silicate and Carbonate Rocks," by W. F. Hillebrand. Department of the Interior, U. S. Geological Survey.

[13] Am. Jour. Sci., 4th Ser., Vol. 14, p. 195, 1903.

and gives an equally sharp end-point. Glucose may be substituted for mannitol. See p. 180.

7. Methanol.—This should be distilled over lime after it has been heated for some hours in contact with the lime under a reflux condenser. The more nearly anhydrous, the methanol (methyl alcohol) is the better.

8. Calcium Chloride.—This should be granular, anhydrous, and free from boron.

Preparation of the Sample

For Minerals.—Chapin used not more than half a gram of mineral powder for even very small amounts of boron, and not less unless the percentage exceeded 10. When the percentage is high it is best to so limit the weight of the sample that the B_2O_3 shall not exceed 0.1 gram. If a flux is used it should be weighed to within a milligram or two; then the amount of acid required to take up the melt can be measured out at once and there is no danger of using too great an excess.

If the mineral is soluble in hydrochloric acid, transfer 1 gram of it to the flask *B*, without letting any adhere to the neck, and treat with not more than 5 ml. of 1 : 1 hydrochloric acid. Heat gently on a water bath until solution is complete.

If the mineral is not soluble, add to it exactly six times its weight of sodium carbonate or of an equi-molecular mixture of sodium and potassium carbonates, mix, and fuse in the usual manner. Without removing from the crucible, decompose the melt with 1 : 1 hydrochloric acid in calculated amount added by degrees. While this is being done the crucible should rest in a casserole, and the lid should be kept in place as much as possible. Toward the end it may be necessary to heat a little, but care should be taken not to boil, for boric acid would be lost with the steam. Pour the solution into the flask *B* and rinse the crucible with a very little water.

Then add pure anhydrous calcium chloride, using about 1 gram for each milliliter of solution and running it through a paper funnel to keep the neck of the flask clean. Twirl the flask a little to allow the chloride to take up the water, connect it with the rest of the apparatus, raise the casserole beneath it until the flask rests in the water but does not touch the bottom, and then begin the distillation of the alcohol from the flask *A*, taking care that the open end of the capillary " boiling tube " is free from alcohol and that the U tube attached to the receiver is trapped with water.

For Water.—Evaporate 2500 ml. to a moist residue in a 1-liter copper beaker, keeping it alkaline to phenolphthalein with saturated sodium hydroxide. Transfer to a 250-ml. Kavalier glass flask, washing the copper beaker finally with 0.1 N hydrochloric acid. This acid may acidify the solution in the flask; if so, make alkaline as before and evaporate to a solid residue. It is not necessary to dehydrate completely. Acidify with concentrated hydrochloric acid; 5 ml. are usually sufficient. Heat to boiling, but avoid evaporation as boron will be lost. Test with indicator to make sure that the contents of the flask are acid. Add one ml. in excess. Add 10 grams of $CaCl_2$ and 50 ml. of methanol (synthetic) and distill as described under " Distillation."

For Plant Materials.—Dry at 70–80 degrees C., grind to a fine powder, and composite. Weigh 10 grams of the material and transfer to a decomposition

flask (Kavalier glass). Add 80 ml. of methanol, 5 to 8 ml. of HCl and 10 grams of $CaCl_2$ (free from boron). Distill as described below. The operations following the distillation are the same for plant material as for waters and will be described in the following paragraphs.

Distillation.—Connect flask *D* containing the sample as shown in Fig. 17A. Flask *S* should contain 10 ml. of 0.5 N NaOH to prevent escape of methyl borate. Start methanol distilling from reservoir *R*. When the contents of *D* are hot, light a small flame under the flask. Try to regulate the heat so that the volume in the flask *D* does not change. Distillation is carried along until 150 to 200 ml. are collected in the receiver *S*. Rinse the contents of the trap tube into *S* and treat the distillate as detailed below.

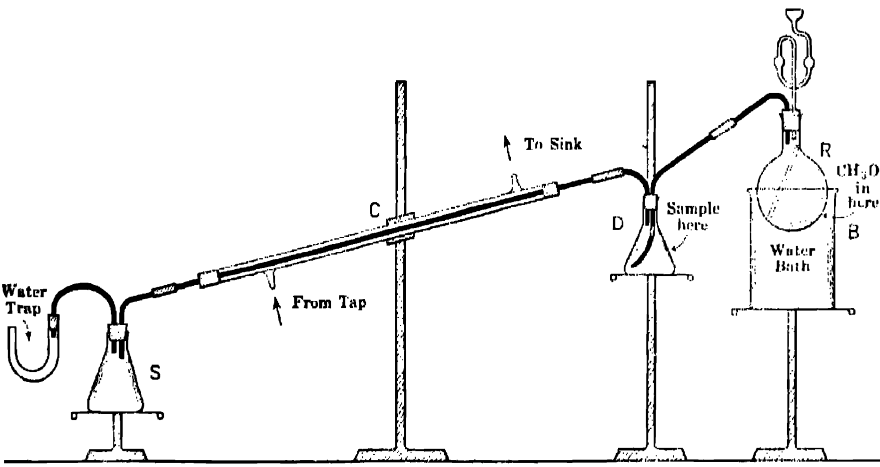


Fig. 17*a*.—Modified Chapin Apparatus.

Treatment of Distillate.—Make the solution alkaline to phenolphthalein, then add 10 ml. of 0.5 N NaOH in excess. Transfer the liquid to a 1-liter copper Kjeldahl flask, not shown in diagram of apparatus, and distill off the methanol. This methanol can be fractionated and used again. Transfer the liquid left in the Kjeldahl flask to a 250-ml. copper beaker, evaporate to dryness, and ignite at a red heat. Add about 10 ml. of water, heat to boiling and, with the aid of a stirring rod having a rubber tip, transfer to a volumetric flask. Then add 7 drops of Sofnol indicator. Make distinctly acid with 2 N HCl. Shake to expel CO_2 and then make distinctly alkaline to phenolphthalein with 0.5 N NaOH. Make up to 110 ml. and filter into another of the 100-ml. flasks. Take an aliquot of 100 ml. of the filtrate, transfer to a 250-ml. Kavalier flask, and proceed with titration as described below.

Titration of Boric Acid.—Make the alkaline filtrate acid to Sofnol with 2 N HCl and then add 5 drops in excess. Boil 3 minutes, shaking the flask occasionally to aid in the expulsion of CO_2. Cool. Titrate as follows: Add CO_2-free 0.5 N NaOH until a slight yellow color of Sofnol shows. Add 1 or 2 drops of 0.1 N HCl. The solution should become pink. Add the standard 0.046 N sodium hydroxide drop by drop until the pink just disappears. The color will be orange not unlike the orange of neutral methyl orange. (If methyl red is used, the neutral color is also orange.) This is the neutral point

for Sofnol and the initial point for titration. Read the burette. Add 1 drop of standard alkali. The indicator should change to a clear lemon yellow. If it does not, one would suspect that carbon dioxide was not completely removed. Continue adding the standard alkali until a reddish color appears, showing phenolphthalein alkalinity. Add about one gram of mannite. The red color will be discharged if boric acid is present. If the red color is discharged, continue adding standard alkali until the red of phenolphthalein reappears. Add another gram of mannite. The color will remain but, if it does not, add more alkali and another gram of mannite until a permanent end point is obtained. This first red color that is permanent in the presence of mannite is the end-point of the titration.

The blank is determined exactly as described above, all of the reagents being used. The author's blanks ranged from 0.45 to 0.60 ml. standard N NaOH.

Calculations.—Milliliters of standard 0.046 N NaOH used between the initial point and the end-point less a blank equals the net titration, which multiplied by 0.5 gives the mg. of boron in the aliquot. In this titration boric acid acts as a monobasic acid. The author used an aliquot of 100/110 of the original sample, so after making this correction the following factors apply:

For 2500-ml. aliquot of water, 1 ml. 0.046 N NaOH equals 0.2 p.p.m.

For a 10-gram aliquot of leaves, 1 ml. 0.046 N NaOH equals 50 p.p.m.

Discussion on the Above Method.—This method for the determination of boron differs from the Chapin method chiefly in the employment of copper flasks and beakers and of Kavalier Bohemian glass flasks for the hot alkaline solutions. Copper beakers are used for the first concentration of the water sample, which must be kept alkaline to prevent the loss of boron by volatilization. Copper Kjeldahl flasks are used when separating the methanol from the alkaline distillate, and finally copper beakers are used in drying and igniting the alkaline residues from the Kjeldahls.

Regarding the Accuracy of the Method.—(*a*) The method seems to be practically quantitative when dealing with pure compounds of boron in amounts not exceeding 5 mg.

(*b*) Where boron is added to a natural water, it is possible to recover from 90 to 95% of the total boron present.

NOTES.—E. T. Allen and E. G. Ziez [14] tested the Chapin method very fully in its application to the determination of boron in glasses and regard it as far superior to other methods, even though it is subject to a slight but very uniform correction of 1 milligram or less, to be determined by a blank run. The correction seems to be due always in part to a boron content of the reagents used and in part to a titration error. The fact that such correction is unavoidable makes the method of uncertain value for determining the very small amounts of boron that rocks may be presumed to carry, but the constancy of results is so great that a consistent excess found over what the blank affords is strong evidence that boron is actually present.

Allen and Ziez found the method to be affected appreciably by relatively large amounts of arsenious acid but not by arsenic acid. The effect of the former can be eliminated by converting it to arsenic acid by oxidizing with hydrogen peroxide after making the solution distinctly alkaline with sodium hydroxide.

[14] "Analysis of Silicate and Carbonate Rocks," by W. F. Hillebrand, Bull. 700, U. S. Geol. Survey, 1919.

Allen and Ziez also found that relatively large amounts of fluorides effect the accuracy of the method but do not seriously impair its usefulness for ordinary work.

Glucose may be used in place of mannite in titrations of borax as shown by LeRoy S. Weatherby and H. H. Chesney (Ind. Eng. Chem., 18, 820, Aug., 1926). Though a larger quantity of glucose (about 10 times) is required than of mannitol, this is of no disadvantage, as a large background of white material is helpful in distinguishing the end-point. As commercial glucose (cerelose) may be obtained at a cost of a few cents a pound, while the price of mannitol is about 200 times as great, the advantage of glucose is seen. (Glucose $3.14 per 100 lbs., mannitol $5.07 per lb., Aug., 1932, quotation.)

The distillation is usually complete when the vapor reaches a temperature of 95° C.

Boron in Plant Materials.—Dry at 70–80° C. Grind to a fine powder. Take 10 grams and treat according to the method described above.

ANALYSIS OF ORGANIC PLANT MATERIALS FOR BORON CONTENT [15]

This procedure,[16] which is a further modification of the Chapin distillation method, may be profitably adapted to the determination of boron in organic material. Boron-free apparatus is used throughout the work. The results, which agree remarkably well, give most favorable returns for boron content, being especially adapted to 1.0–500 mgs. of B_2O_3. With the aid of H_2SO_4 and MeOH it is possible to remove all B_2O_3 by distilling off the Me ester. A 10 gram sample is taken and placed in a liter Kavalier flask and digested with concentrated H_2SO_4, water then added; methanol and the methyl borate distilled according to Chapin's method. Two distillations suffice for the complete removal of all boric oxide. Contacting CO_2-free NaOH in the receiving flask the distillate is carefully evaporated in a silver dish which serves to oxidize any SO_2 that may have been evolved. The residue is then fused to destroy formates or other organic matter. Titration completes the process, using HCl and CO_2-free NaOH with Sofnol Red No. 1 as a preliminary indicator and employing glucose [17] or mannitol and phenolphthalein as final indicators.

Note.—(by W. W. Scott)—Methods appearing in this chapter have been checked in the laboratory. The Editor acknowledges assistance and contributions from Messers Russell G. Dressler, Arthur Zeismer, Howard W. Olson,

[15] Modification of the Schulek and Vastagh boric acid adaptation as developed by Lester K. Gates and W. W. Scott at the University of Southern California.

[16] Schulek and Vastagh, "Zeitschrift Anal. Chim.," 84, 167, 1931.

[17] Glucose (cerelose) can be accurately substituted for mannitol here. Though requiring ten times as much glucose as mannitol, the cost of the latter is 200 times as great.

Lester K. Gates, Glen E. Cline and certain Industrial Laboratories. Dr. W. H. Chapin examined the manuscript before publication and made several valuable suggestions.

ANALYSIS OF BORON CARBIDE[18]

BORON

Preparation of Standard Solutions.—.2 N and .10 N solutions of NaOH are needed. They must be carbonate free. To prepare them proceed as follows:

Dissolve 75 grams of c.p. NaOH in 75 ml. of water. Pour into a large test tube or similar tall vessel and allow to stand several days or until all solid matter settles. Of the clear solution use 12 ml. per liter for the .2 N NaOH and 6 ml. per liter for the .10 N NaOH. Dilute with water that has been boiled and cooled to rid it of CO_2.

Titrate a 25 ml. portion of each solution with a standard acid and methyl red indicator, calculate and make the necessary dilutions with CO_2 free water to bring the solutions to their respectively desired normalities, and standardize them accurately against pure, anhydrous B_2O_3 glass.

Standardization of the Solutions.—Fuse c.p. boric acid thoroughly and store the resulting B_2O_3 glass in a well stoppered bottle. If the boric acid at hand is not considered pure enough, recrystallize it twice from hot water before fusing.

For standardizing the .2 N solution use approximately .3000 gram of the glass. For the .10 N solution use .1500 gram.

Weigh the sample roughly into a clean, ignited and weighed platinum crucible. Cover the crucible tightly, ignite for five minutes at a good red heat, cool and weigh again to get the weight of the sample. Dissolve the sample from the crucible with 50 ml. of CO_2 free water, add 4 drops of paranitrophenol, 1 ml. phenolphthalein and titrate with the alkali being standardized, using mannite to obtain the end point. One gram of mannite is added at the start of the titration and further one gram additions are made as needed while approaching the end point.

Four samples should be treated in the above manner for each solution. Divide the weight of each sample by the number of ml. used for its titration and if the four results show satisfactory agreement, average them and take the result as the B_2O_3 value per ml. of the solution. The B_2O_3 value multiplied by .31074 gives the B value per ml. of the solution.

Indicators.—Paranitrophenol: Dissolve one gram in 100 ml. denatured alcohol.

[18] Method used by the Norton Company, Worcester, Mass. supplied by the courtesy of M. O. Lamar.

Phenolphthalein: Dissolve one gram in 200 ml. denatured alcohol.

Blanks.—Weigh and treat four B_2O_3 glass samples as in standardizing up to the point where they are dissolved in water. Wash off the crucibles thoroughly, keeping the volumes of the solutions at approximately 100 ml. Acidify the solutions distinctly with 1–1 HCl and treat them as in the method next to be described, up to and through the main titration with .2 N NaOH.

The main titrations with the .2 N NaOH will show amounts of B_2O_3 slightly larger than the weights of the samples. Average these slight excesses, calculate their value in terms of ml. of the standard solution, and subtract this value from all main titrations when analyzing samples.

This blank might be taken care of by taking the original samples through the method, but the above procedure gives such very satisfactory results that it is adhered to.

For the blank on the small recovery titration with the .10 N NaOH a new solution is made up and titrated exactly as in the recovery part of the method. This blank is large when compared with the small amounts of B_2O_3 obtained in the recoveries but it is very consistent.

The Method.—Weigh .12 gram of the sample into a platinum crucible. Mix thoroughly with Na_2CO_3 and cover with a layer of the carbonate, using 1 gram in all. Cover the crucible tightly and fuse slowly with gradually increasing temperature, finishing with a temperature as low as is consistent with complete fusion. Remember that during fusion there is always danger of volatilizing boric acid, and care must be used in performing the operation. When fusion is complete spread the melt on the inside of the crucible walls, allow to cool and place the crucible and cover in a 250 ml. beaker. Add 50 ml. of water and allow the melt to dissolve. Heat may be used to hasten solution but it should be used sparingly with the beaker well covered. Do not boil.

When solution is complete wash off the crucible and cover keeping the solution in the beaker down to 100 ml. Acidify with 7 to 8 ml. of 1–1 HCl and add four drops of paranitrophenol. Dilute one volume of the strong NaOH stock solution used in making the standard solutions with one volume of water and by means of it and a medicine dropper bring the solution in the beaker nearly to the neutral point. Complete the neutralization to the paranitrophenol end point with the .2 N standard NaOH.

When the iron in the solution amounts to about two milligrams or over its color appears and deepens as neutralization is approached and may be mistaken for the indicator end point. This must be guarded against as under neutralization ruins the analysis. Several drops over the end point do no harm, so make sure that neutralization is complete.

Cover the beaker and heat, *do not boil*, just until the precipitate coagulates. Stir in one quarter of a Whatman 7 cm. 41 filter paper macerated to pulp. Filter through a 7 cm. 41 Whatman filter paper, wash the beaker three times and give the precipitate six thorough washings on the paper. Catch the filtrate in a suitable pressure flask. If the precipitate is small hot water is satisfactory for washing, but if it amounts to four or five milligrams or more a hot 1% solution of sodium chloride must be used to prevent hydrolysis. Set this main filtrate aside for titration.

Place the original beaker under the funnel and dissolve the precipitate through the paper by dropping hot 1–1 HCl on it. It does not take much of

the acid to do this but make sure no undissolved precipitate remains mixed with the pulp. Wash the filter and pulp six times with hot water or 1% NaCl solution, add four drops of paranitrophenol, and repeat exactly the first precipitation and filtration, this time catching the filtrate in a 500 ml. Erlenmeyer flask. This filtrate contains the recovery titration. Before starting the filtration the small wad of pulp in the filter is carefully removed and stirred into the precipitate in the beaker.

Acidify the main filtrate in the pressure flask with 1–1 HCl adding about three drops in excess. Warm the flask on a pan of sand until the solution is about 40° C., transfer the flask still on the sand bath to a suction pump and boil under reduced pressure until bubbles cease to come from the solution. Perform this operation carefully to avoid loss by splashing. Disconnect the flask, cool it in running water and thoroughly wash down the stopper and inside of the flask with CO_2 free water. Nearly neutralize the solution with strong carbonate free NaOH and finish the neutralization with the .10 N NaOH standard solution. In the solution as here prepared this end point is very sharp and one drop of the .10 N solution will give it distinctly, especially if the flask is examined at eye level toward a window between the additions of the last few drops.

When the solution has been adjusted to the neutral point add one ml. of phenolphthalein indicator and a gram of mannite. Begin the titration with the .2 N NaOH and continue until the pink color of the phenolphthalein indicator develops. Add another gram of mannite and again develop the pink color. Continue these additions of mannite until the last one has no effect on the fully developed pink color. As this end point is properly obtained only through familiarity with it, an attempt is made to describe its approach. As the end of the titration nears, the pink color persists more and more when mannite is added. First a pink tinge will persist even though the yellow is greatly restored. After the next addition the pink will remain decidedly, mixed with the yellow color. Finally a stage will be reached where the pink color only lightens upon the addition of mannite. No yellow being discernible. When this stage is reached one or two drops of the .2N solution will give a sudden, definite, fully developed pink color that will remain for hours after the addition of another gram of mannite. This is the end point.

Now make the recovery titration on the solution in the Erlenmeyer flask in the same manner, except that the .10 N NaOH solution is used, and as no CO_2 is present the solution is not boiled under reduced pressure. This end point is not difficult to obtain.

Subtract the respective blanks from each titration. Multiply each titration by the B value per ml. of the solution used. Add the B values together, divide by the weight of the sample and multiply by 100 to obtain the percentage of B in the sample.

SILICA

Weigh .5 gram of the sample and 8 grams of Na_2CO_3. Mix the sample thoroughly in a platinum crucible with most of the carbonate and cover the mixture with the remainder. Fuse with gradually increasing temperature. Use the highest heat of the burner only if the last bits of the sample do not fuse at a moderate heat.

Run the melt up on the walls of the crucible and cool. Place the crucible and cover in a casserole and leach the melt with water. Acidify the solution with 25 ml. strong HCl, wash off the crucible and cover, add 25 ml. methyl alcohol and evaporate slowly to dryness with the casserole uncovered. Evaporate twice more with 5 ml. of HCl and 25 ml. of methyl alcohol. If boric acid remains condensed on the sides of the casserole, evaporate a third time.

When boric acid is no longer evident, cool the casserole, moisten the residue with 10 ml. 1-1 HCl, add 50 ml. hot water and warm until all soluble salts are in solution. Filter, wash the precipitate with hot 2% HCl five times, then five times with hot water. Return the filtrate to the casserole and repeat the dehydration and filtration.

Burn off both papers in a platinum crucible, ignite intensely for 20 minutes, cool and weigh. Add a few drops of water, two drops of strong H_2SO_4, and 5-10 ml. of HF. Evaporate until both acids are gone, ignite the crucible and residue for five minutes, cool and weigh. The loss in weight represents the silica. This weight divided by the weight of the sample and multiplied by 100 gives the percentage of silica in the sample.

We do not encounter high silica in boron carbide samples, but if silica should be encountered much over 5% there is danger of it being contaminated with boric acid in spite of the evaporations with alcohol. In such a case, after the first ignition of the silica, fuse it with one to two grams of sodium carbonate, make two dehydrations with intervening filtration as above, then ignite, weigh, and finish as directed. No alcohol is necessary in these dehydrations.

OTHER CONSTITUENTS

Iron, aluminum, calcium, and magnesium are determined in the filtrate from the silica determination. Carbon is determined by combustion with a red lead flux. Refer to the analysis of silicon carbide, where instructions for making these determinations are given in great detail.

NOTES.—This is a very exacting analysis; especially the determination of boron. In this determination the analyst is placed in a disadvantageous position. The sample operated upon is small and the percentage determined is large. This multiplies any errors greatly, so that errors must be held to an absolute minimum.

The B_2O_3 used for standardizing must be pure, completely anhydrous, and properly weighed. The operations of standardizing solutions and obtaining blanks must be performed with the utmost care. All titration end points must be obtained with precision, and last but far from least absolutely clean glassware must be used, especially burettes. "Ordinarily" clean glassware will not do.

DETERMINATION OF MINUTE AMOUNTS OF BORON[19]

This excellent colorimetric method, comparable with the Gutzeit method for arsenic, is specially adapted to the determination of boron present in minute amounts in soils, without the necessity of using exceedingly large samples, which are required by the Chapin, Gooch and Jones and similar methods involving gravimetric or volumetric procedures. The reagents that are required can be rapidly prepared and the apparatus necessary easily procurable from ordinary laboratory stock. The procedure is suitable for quantities of B_2O_3 ranging from 0.1 to 0.005 mg. Larger amounts may be determined by using larger vials and longer strips of turmeric paper. The method depends upon the length of stain produced by the action of boracic acid on turmeric paper, comparison being made with standard stains produced by known amounts of boron under similar conditions.

Reagents. *1. Hydrochloric Acid, Sp. Gr. 1.162.*

2. Phosphoric Acid.

3. Sodium Carbonate, 1 Normal.

4. Methyl Alcohol (Methanol), Absolute, C. P.

5. Turmeric Solution.—Add an excess of turmeric powder to 95% alcohol and filter.

6. Turmeric Paper.—A good grade of filter paper was soaked in a solution of turmeric, the excess of solution squeezed out, and the papers dried. The saturation must be as uniform as possible.

7. Standard Borate Solution.—Dissolve 0.2739 g. of $Na_2B_4O_7 \cdot 10H_2O$ in water to make a liter of solution. One ml. of this solution contains 0.1 mg. of B_2O_3.

Apparatus.—*A*. A distilling flask of 250 ml. capacity, supported on a water bath, with a one-holed stopper carrying a long-stemmed funnel of 50 ml. capacity.

B. Water-cooled condenser 40 cm. long.

C. Platinum dish of 60 ml. capacity.

D. Platinum crucible of 25 ml. capacity.

E. Glass vials 30 mm. high and 6 mm. in diameter.

F. Glass vials 60 mm. high and 12 mm. in diameter (for larger quantities of boron).

Procedure.—Leach 100 g. of soil with 200 ml. of distilled water and evaporate the leachate to dryness in a platinum dish on a water bath. Add a small amount of sodium carbonate and ignite the mixture to remove organic matter. (The dish must be covered to prevent loss of material.) To the cool residue add 10 ml. of phosphoric acid and transfer the solution to the distilling flask. Rinse the platinum dish with 20 ml. of methyl alcohol used in two or three portions and add these washings to the distilling flask. Distill from a water bath and collect the distillate in a platinum dish of not less than 60 ml. capacity (this size is necessary to prevent mechanical loss in the subsequent evaporation of the alcohol) which contains four to six drops of normal sodium carbonate solution.

[19] Modification and adaptation of the Bertrand and Agulhon method as developed by (Mrs.) Sondheim Keaton Webb and W. W. Scott at U.S.C.

After about twenty minutes when the distillation has practically ceased, remove the flame, and add 10 ml. of alcohol through the dropping funnel. (The use of the dropping funnel saves time as it precludes the necessity of cooling the mixture in the distilling flask before the alcohol can be added.) Proceed with the second distillation until distillate stops coming over. If the directions have been carefully followed and the proper precautions taken to assure the absence of water, all the boron will be recovered in these two operations. To test for complete recovery of the boron, a drop of the distillate may be collected on a piece of turmeric paper, a drop of dilute hydrochloric acid added and the paper dried on a watch glass over a water bath. A pink coloration indicates the presence of boron. If boron is present, add 10 ml. of methyl alcohol and distill again.

The combined distillates are evaporated to dryness on a water bath. Keep the bath below boiling. After the distillates have evaporated down to about 5 ml., transfer the remaining liquid to the 25-ml. platinum crucible, washing out the first dish with a few milliliters of methyl alcohol, and evaporate the whole to dryness. This transfer to the smaller dish is essential because the quantity of solvent subsequently used is not sufficient to remove the residue quantitatively from the larger dish.

To the cool residue add four drops of hydrochloric acid, sp.gr. 1.162, and 0.5 ml. of distilled water. Transfer to a vial 30 mm. high, rinsing several times with water, and dilute to 2 ml. as shown by a mark on the vial. Immerse a piece of turmeric paper (45 by 3 mm.) in the liquid to a depth of 15 mm. and allow it to soak three hours at a temperature of 35° C. or 24 hours at room temperature. (The former is preferred as it gives a more clearly defined coloration.) The height in millimeters of the red color thus produced is compared against a series of standard papers prepared by soaking strips of turmeric paper in solutions containing known amounts of boron treated in the same manner.

DETERMINATION OF TRACES OF BORON IN IRRIGATION WATERS

Samples of water must be gathered in containers that are absolutely boron free. Most glass ware is unsatisfactory because of the recent extensive use of borax in its manufacture. Tin or copper containers are satisfactory. The amount of the sample required for each analysis depends upon the amount of boron present. 500 ml. will give a measurable amount of boron for most irrigation waters. The size of the sample may be regulated by preliminary runs.

The sample is evaporated almost to dryness over a water bath in a silica dish. The moist residue is transferred to a platinum crucible, a few drops of

sodium carbonate are added and the whole evaporated to dryness. The residue is then ignited to destroy organic matter. From this point, the procedure for the determination of minute amounts of boron in soils may be followed, as stated in the preceding method.

NOTES.—In the evaporation of the methyl alcohol distillate, G. E. Cline found the evaporation proceeds at a satisfactory rate if the crucible is placed on the outer edge of the water bath, on the metal cover, and the water in the bath allowed to boil.

The first evaporation may be hurried by evaporating at a higher temperature, if sodium carbonate is added to keep the solution basic, and the container covered to avoid loss by spattering.

Estimation of Borate in Natural Waters.—The method is based on the color produced by a borate on turmeric. The following details are taken from the method outlined by Margaret D. Foster.[20]

Reagents. ***Standard Borate Solution.***—(1) 0.16 g. borax in 1 liter of pure water (1 ml. contains 0.1 mg. BO_3). (2) twenty-five ml. diluted to 250 ml. (1 ml. contains 0.01 mg. BO_3).

Turmeric Solution.—Five grams of thoroughly washed turmeric are dissolved in 500 ml. of alcohol and filtered before use.

Hydrochloric Acid Solution.—Four ml. HCl (sp.gr. 1.178–1.183) added to 96 ml. of pure water.

Salt Solution.—Twenty-five grams of NaCl and 25 grams Na_2SO_4 (anhyd.) in 1 liter of pure water.

Procedure.—Ten ml. of the sample is placed in a small white evaporating dish and 1 ml. of the HCl solution and 1 ml. of the turmeric reagent added. The dish is placed on a steam bath and the solution evaporated to dryness. A golden colored residue indicates the absence of a borate; a faint pink or rose tint shows the presence of a borate. The intensity of color increases with the amount of borate and a quantitative estimation can be made by comparing with a series of standards made by taking known amounts of standard borate solution, adding the reagents above and taking to dryness in evaporating dishes. The standards may range from 0 to 0.5 mg. BO_3. The suggested standards contain 0.0025, 0.005, 0.0075, 0.01, 0.03, 0.1, 0.25, 0.5 mg. BO_3 respectively. If the color is too intense 0.5 ml. of turmeric solution is added to both standard and sample.

NOTES.—See also "Determination of Boron in Natural Waters and Plant Materials" by L. V. Wilcox, Ind. Eng. Chem., Anal. Ed. 2, 358, 1930. The water (alkaline to phenolphthalein) is evaporated and the boron converted to methyl borate and determined by the Chapin method.

[20] U. S. Geological Survey. Ind. Eng. Chem., Anal. Ed. 1, 27, 1929.

BROMINE

Br, ***at.wt.*** **79.916;** ***sp.gr.*** **3.1883°;** ***m.p.*** **− 7.3°;** ***b.p.*** **58.7° C.;** ***acids,*** **HBr, HBrO, $HBrO_3$**

Bromine occurs only in combination, generally associated with the alkaline earths and the alkalies and is accordingly found in salt deposits, mineral springs and sea water and is a by-product of the salt industry. It is found in marine plants; traces occur in coal, hence it is found in gas liquors.

DETECTION

Silver Nitrate solution precipitates silver bromide, AgBr, light yellow, from solutions containing the bromine anion. The precipitate is insoluble in dilute nitric acid, but dissolves with difficulty in ammonium hydroxide and is practically insoluble in ammonium carbonate solution (distinction from AgCl).

Carbon Disulfide or Carbon Tetrachloride shaken with free bromine solution, or with a bromide to which a little chlorine water has been added (a large excess of chlorine must be avoided, as this forms BrCl compound), will absorb the bromine and become a reddish-yellow color, or if much bromine is present, a brown to brownish-black. In the latter case a smaller sample should be taken to distinguish it from iodine.

Bromates are first reduced by a suitable reducing agent such as cold oxalic acid, sodium nitrite, hydrochloric acid, etc., and the liberated bromine tested as directed above. *Silver nitrate* added to bromates in solution precipitates $AgBrO_3$, which is decomposed by hydrochloric acid to bromine gas.

Magneta Test for Bromine.[1]—The test reagent is made by adding 10 ml. of 0.1% solution of magenta to 100 ml. of 5% solution of sulfurous acid and allowing to stand until colorless. This is the stock solution. Twenty-five ml. of this reagent is mixed with 25 ml. of glacial acetic acid and 1 ml. of sulfuric acid. Five ml. of this is used in the test.

[1] G. Denigès and L. Chelle. Ann. chim. anal., **18**, 11–15, 1913; Analyst, **38**, 119, 1913.

NOTE.—Bromine was first isolated from the salts of the waters of the Mediterranean by Balard in 1826. The element is a valuable laboratory reagent used for oxidation purposes. Its silver salt is used in photography. The bromides find application in medicine.

Test.—Five ml. of the magenta reagent is mixed with 1 ml. of the solution tested. Chlorine produces a yellow color. Bromine gives a reddish-violet coloration. The colored compound in each case may be taken up with chloroform or carbon tetrachloride and a colorimetric comparison made with a standard.

In halogen mixtures, iodine is first eliminated by heating with a ferric salt. Bromine is now liberated by adding sulfuric acid and potassium chromate. A glass rod with a pendant drop of sodium hydroxide is held in the vapor to absorb bromine, and the drop then tested with the magenta reagent. After iodine and bromine are eliminated, chlorine may be tested by heating the substance with potassium permanganate, which liberates this halogen.

ESTIMATION

In the preparation of the sample for analysis it should be recalled that silver bromide is but slightly soluble so that, in presence of silver, bromine will be left with the silica residue. The preparation of the sample and the methods of estimation are very similar to those of chlorine.

PREPARATION AND SOLUTION OF THE SAMPLE

The following facts regarding solubility should be remembered: The element bromine is very soluble in alcohol, ether, chloroform, carbon disulfide, carbon tetrachloride, concentrated hydrochloric acid and in potassium bromide solution. One hundred ml. of water at 0° C. is saturated with 4.17 grams of bromine, and at 50° C. with 3.49 grams. The presence of a number of salts increases its solubility in water, e.g., $BaCl_2$, $SrCl_2$, etc.

NOTE.—The element is a dark, brownish-red, volatile liquid, giving off a dark reddish vapor with suffocating odor, irritating the mucous membrane (antidote dil. NH_4OH, ether), very corrosive. Acts violently on hydrogen, sulfur, phosphorus, arsenic, antimony, tin, the heavy metals, and on potassium, but has no action on sodium, even at 200° C. Bleaches indigo, litmus, and most organic coloring matter. It is a strong oxidizing agent. Bromine displaces iodine from its salts, but is displaced by chlorine from its combinations.

Bromides are soluble in water, with the exception of silver, mercury, lead, and cuprous bromides.

Bromates are soluble in water with the exception of barium and silver bromates and some basic bromates.

Decomposition of Organic Matter for Determination of Bromine.—The substance is decomposed with nitric acid in presence of silver nitrate in a bomb

combustion tube by the Carius method described in the chapter on Chlorine, under "Preparation and Solution of the Sample." The residue, containing the halides, is dissolved in warm ammonia water, and filtered, as stated. The filtrate and washings are acidified with nitric acid, heated to boiling and the silver bromide settled in the dark, then filtered through a weighed Gooch crucible, the washed precipitate dried at 130° C. and weighed as AgBr.

In presence of two or three halogens the lime method is recommended, as given in the chapter on chlorine.

Salts of Bromine.—The ready solubility of bromides and bromates has been mentioned. A water extract is generally sufficient. Insoluble salts are decomposed by acidifying with dilute sulfuric acid and adding metallic zinc. The filtrate contains the halogens.

SEPARATIONS

Separation of Bromine from the Heavy Metals.—Bromides of the heavy metals are transposed by boiling with sodium carbonate, the metals being precipitated as carbonates and sodium bromide remaining in solution.

Separation of Bromine from Silver (AgBr) and from Cyanides (AgCN).—The silver salts are heated to fusion. The mass is now treated with an excess of zinc and sulfuric acid, the metallic silver and the paracyanogen filtered off and the bromine determined in the filtrate.

Separation of Bromine from Chlorine or from Iodine.—Details of the procedure for determining the halogens in presence of one another is given in the chapter on Chlorine, page 276. Free bromine is liberated when the solution of its salt is treated with chlorine.

Separation of Bromine from Iodine.[2]—The neutral solution containing the bromide and iodide is diluted to about 700 ml. and 2 to 3 ml. of dilute sulfuric acid, 1 : 1, added, together with about 10 ml. of 10% sodium nitrite, $NaNO_2$, solution. (Nitrous acid gas may be passed through the solution in place of adding sodium nitrite, if desired.)[3] The solution containing the halides is boiled until colorless and about twenty minutes longer, keeping the volume of solution above 600 ml. 0.5 gram KI may be decomposed and the iodine expelled from the bromide in half an hour. The bromine is precipitated from the residue remaining in the flask by addition of an excess of silver nitrate and determined as silver bromide.

The procedure for determining iodine is given in the chapter on this subject.

[2] F. A. Gooch and J. R. Ensign, Am. Jour. Sci., (3), xl, 145.

[3] Nitrous acid gas is generated by dropping dilute H_2SO_4, by means of a separatory funnel onto sodium nitrite in a flask.

GRAVIMETRIC METHODS

PRECIPITATION AS SILVER BROMIDE

The general directions for determination of hydrochloric acid and chlorides apply for determining hydrobromic acid and bromides.

I. Hydrobromic Acid and Bromides of the Alkalies and Alkaline Earths.

Procedure.—The bromide in cold solution is made slightly acid with nitric acid and then silver nitrate added slowly with constant stirring until a slight excess is present. The mixture is now heated to boiling and the precipitate settled in the dark, then filtered through a weighed Gooch crucible, and washed with water containing a little nitric acid and finally with pure water to remove the nitric acid. After ignition the silver bromide is cooled and weighed as AgBr.

$$AgBr \times 0.4256 = Br, \quad \text{or} \quad \times 0.6337 = KBr.$$

II. Heavy Metals Present.

If heavy metals are present it is not always possible to precipitate silver bromide directly. The heavy metals may be removed by precipitation with ammonia, sodium hydroxide or carbonate and the bromide then determined in the filtrate as usual.

VOLUMETRIC METHODS

Free hydrobromic acid may be titrated with standard alkali exactly as is described for the determination of hydrochloric acid in the chapter on Acids. One ml. normal caustic solution is equivalent to 0.08092 gram HBr.

DETERMINATION OF FREE BROMINE. POTASSIUM IODIDE METHOD

The method depends upon the reaction $KI + Br = KBr + I$.

Procedure.—A measured amount of the sample is added to an excess of potassium iodide, in a glass-stoppered bottle, holding the point of the delivering burette just above the potassium iodide solution. The stoppered bottle is then well shaken, and the liberated iodine titrated with standard thiosulfate solution.

One ml. of N/10 thiosulfate, $Na_2S_2O_3 = 0.007992$ gram Br.

DETERMINATION OF BROMINE IN SOLUBLE BROMIDES. LIBERATION OF BROMINE BY ADDITION OF FREE CHLORINE

When chlorine is added to a colorless solution of a soluble bromide, bromine is liberated, coloring the solution yellow. At boiling temperature the bromine is volatilized, the liquid becoming again colorless. When the bromide is completely decomposed and bromine expelled, further addition of chlorine produces no color reaction. $KBr + Cl = KCl + Br$.

Procedure.—The solution containing the bromide is heated to boiling and standard chlorine water added from a burette (protected from the light by being covered with black paper), the tip of the burette being held just above the surface of the hot bromide solution to prevent loss of chlorine. The reagent is added in small portions until finally no yellow coloration is produced. From the value per ml. of the chlorine reagent the bromine content is readily calculated.

Standard Chlorine Water.—The reagent is made by diluting 100 ml. of water saturated with chlorine to 500 ml. This solution is standardized against a known amount of pure potassium bromide (dried at 170° C.), the same amount of bromide being taken as is supposed to be present in the solution examined. The value per ml. of the reagent is thus established.

SILVER THIOCYANATE-FERRIC ALUM METHOD (VOLHARD)

The procedure is the same as that used for the determination of chlorine. The bromide solution is treated with an excess of tenth-normal silver nitrate solution, and the excess of this reagent determined by titration with ammonium thiocyanate, using ferric alum indicator. One ml. of the thiocyanate should be equivalent to 1 ml. of silver nitrate solution. The formation of the red ferric thiocyanate indicates the completed reaction. (Consult the procedure in the chapter on Chlorine, page 271.)

$$\text{One ml. of } N/10\ AgNO_3 = 0.007992 \text{ gram Br.}$$

NOTE. **Eosin Adsorption Indicator in Halide Titrations.**—Titration of bromide with silver nitrate in presence of the adsorption indicator, eosin, is of interest. The dyestuff is adsorbed by the silver bromide with formation of a dark-red colored substance. The titration may be made in feebly acid solution as 0.1 N nitric acid solution or in acetic acid solution, using 2–5 drops of a 0.5 eosin (sodium) in water solution per 10 ml. of 0.1 N halide solution. More dilute solutions may be titrated—i.e., 1–2 drops of the indicator per 25 ml. of 0.01 N halide solution. The color of the indicator changes to a bluish hue and the silver halide separates out with an intense rose-red color. In 0.001 N solutions the color changes from rose to a purplish red.

DETERMINATION OF TRACES OF BROMINE

(1) By means of the magenta reagent, described under "Detection," small amounts of bromine may be determined colorimetrically.

To 5 ml. of the solution is added 0.2 ml. of conc. hydrochloric acid, 1 ml. of concentrated sulfuric acid, 1 ml. of the stock magenta reagent and 0.2 ml.

of a 10% solution of potassium chromate, shaking the mixture with addition of each reagent, and without cooling, 1 ml. of chloroform is added. Comparison is made with a standard sample containing a known amount of bromide.[4]

NOTE.—A solution containing 0.001 gram bromine per liter has a violet to reddish-violet color.

(2) **Bromination of Phenol Red.**[5] **Procedure.**—(*a*) 0–4 gamma range. To 1 ml. of neutral sample add 0.05 ml. of phenol red (1 mg. per 10 ml.) and 0.2 ml. of saturated borax solution. Add 0.2 ml. of 0.01 N calcium hypochlorite (H. T. H.; solution filtered), and let stand exactly four minutes with occasional shaking; then add 0.05 ml. of 0.1 N sodium arsenite, followed by 0.20 ml. of acetate buffer (30 ml. glacial acetic acid and 68 g. of sodium acetate per liter). The color will be yellow with less than 1 gamma Br, reddish with 1.5–2 and blue violet above 2.5 gamma.

(*b*) Range 3–18 gamma Br. The same procedure (*a*) is used with the following quantities: 10 ml. sample; 0.2 ml. phenol red, 2 ml. borax, 0.2 ml. 0.1 N hypochlorite, 0.5 ml. arsenite and 1.5 ml. of acetate buffer. Compare with fresh standards prepared in the same manner.

NOTES.—Ammonium salts and other reducing agents interfere with the action of the hypochlorite and are to be removed or oxidized. Iodide is removed by oxidation with nitrous acid: Treat 10–15 ml. of solution containing 60 mg. of iodide or less with 2 ml. of n H_2SO_4 and 1 ml. 0.5 M $NaNO_2$. Boil to expel iodine and replace the water lost by evaporation.

Chlorides in any amount do not interfere.

DETERMINATION OF BROMATES BY REDUCTION WITH ARSENIOUS ACID AND TITRATION OF THE EXCESS[6]

Bromic acid may be reduced by arsenious acid in accordance with the reaction $3H_3AsO_3 + HBrO_3 = 3H_3AsO_4 + HBr$. In the process a considerable excess of arsenious acid is added, the excess titrated with iodine and the bromate calculated.

Procedure.—The sample of bromate, dissolved in water, is treated with a considerable excess of N/10 arsenious oxide (dissolved in alkali hydrogen carbonate) reagent, the solution then acidified with 3 ml. to 7 ml. of dilute sulfuric acid (1 : 1) and diluted to a volume not exceeding 200 ml. After boiling for ten minutes, the free acid is neutralized with alkali hydrogen carbonate ($NaHCO_3$ or $KHCO_3$) and the excess of arsenite titrated with N/10 iodine.

[4] G. Denigès and L. Chelle, Ann. chem. anal., **18**, 11–15, 1913; Analyst, **38**, 119, 1913. By means of the magenta reagent it is possible to detect bromine in the ash of plants, beet root, spinach, etc. The organic substance may be decomposed by heating in a combustion tube. Filter paper moistened with the reagent and held in the fumes of the organic substances gives the characteristic test if bromine is present.

[5] Stenger and Kolthoff, J. Am. Chem. Soc., **57**, 831 (1935).

[6] Method of F. A. Gooch and J. C. Blake, Am. Jour. Sci., **14**, Oct., 1902.

Let x ml. equal the difference between the two titrations with N/10 iodine (i.e. of total arsenite minus excess arsenite) and w equal the weight of bromate desired, then

$$w=\left(\frac{x\text{ ml.}\times\text{mol. wt. }RBrO_3}{6\times10\times1000}\right)\text{milligrams.}$$

ANALYSIS OF CRUDE POTASSIUM BROMIDE AND COMMERCIAL BROMINE

DETERMINATION OF CHLORINE, COMBINED OR FREE

This is the principal impurity present and its estimation is concerned here. Andrews' modification of Bugarszk's method [7] is as follows:

Procedure.—The following amount of sample and reagents should be taken.

Approx. Percent Impurity if KCl Present is	Amount Substance to be Taken, Gram	Iodate Solution 1/5 N Required: ml.	2N HNO_3 Required, ml
Over 5	0.6	36	20
1.5 to 5	1.8	96	26
0.2 to 1.5	3.6	186	35

The mixture is gently heated to boiling in a long necked Kjeldahl flask, inclined at an angle of 30°, potassium iodate solution added, then nitric acid and sufficient water to make the volume about 250 ml. The boiling is continued until bromine is expelled (test steam with 2% KI solution rendered faintly acid with hydrochloric acid). The mixture is boiled down to not below 90 ml. Now 1 to 1.5 ml. of 25% phosphorus acid are added and the mixture boiled for five minutes after all the iodine has been expelled. The colorless liquid is cooled, mixed with a slight excess of 1/20 or 1/50 normal silver nitrate solution (according to the proportion of chloride), the excess of silver nitrate then determined by titration with standard thiocyanate with ferric nitrate as indicator. (See procedure for silver thiocyanate-ferric alum method of Volhard for determination of chlorine, page 271.)

DETERMINATION OF CHLORINE IN CRUDE BROMINE

Three grams of bromine (or more if less than 0.5% chlorine is present) in 50 ml. of 4% potassium iodide solution in a glass-stoppered flask (cooled in ice

[7] J. Am. Chem. Soc., **29**, 275–283, 1907; Z. anorg. Chem., **10**, 387, 1895.

during hot weather) are shaken and then transferred to a Kjeldahl flask. Sixty ml. of 1/5 N KIO_3 solution and 24 ml. 2N HNO_3 introduced, the solution diluted to 250 ml. and chlorine determined as directed above.

All commercial bromine contains chlorine. The U. S. Bureau of Standards determines the composition from the specific gravity of the two.

DETERMINATION OF BROMINE IN MINERAL WATERS IN PRESENCE OF IODINE. SEPARATION FROM IODINE

The method of Baughman and Skinner (U. S. Bureau of Chemistry) is as follows:

The neutral or slightly acid sample, which should contain not more than 0.1 g. bromine, or 10 g. total salts, is introduced into the distillation flask and adjusted to a volume of approximately 75 ml. One and a half to 2 grams of ferric sulfate are added, the liberated iodine distilled with steam into 100 ml. of potassium iodide solution (10 g. KI per 100 ml.). The potassium iodide solution may be titrated with sodium thiosulfate solution to determine the iodine. The bromine is determined in the liquid remaining in the distillation flask.

DETERMINATION OF BROMIDE IN MINERAL WATERS AND BRINES[8]

Bromine occurs combined as bromide in natural and artificial brines, associated frequently with small amounts of iodide. Bromine may be obtained in the mother liquor or "bittern," a by-product in the manufacture of common salt. The following procedure for evaluation of these brines for their bromine content was developed by W. F. Baughman and W. W. Skinner, U. S. Bureau of Chemistry.

Apparatus.—Three tall form, 250-ml. glass stoppered Dreschsel gas washing bottles or cylinders are joined together in series, the first two being joined by welding together the outlet tube of the first and the intake tube of the second, and the second and third by rubber tubing, bringing the ends of the glass tubing in contact with each other. The drawing Fig. 18 shows the details of the apparatus.

Procedure.—"Evaporate the sample of water or brine, which should not be acid (if necessary add a small amount of sodium carbonate), to dryness or nearly so. Charge the reaction cylinder by introducing first glass beads to a depth of about 1 in., then as much of the sample as can be scraped in, and finally enough glass beads to fill the cylinder half full. Make a solution of sodium sulfite and sodium carbonate of such a concentration that 25 ml. will contain 1 g. of sulfite and 0.2 g. of carbonate. Add 20 ml. of this solution to the first absorption cylinder, 5 ml. to the second, and dilute each to approximately 200 ml. Connect the three cylinders and draw through a slow current of air. Add 15 g. of chromic anhydride dissolved in 10 to 12 ml. of water to the reaction cylinder, followed by washings from the evaporating dish which contained the sample, sufficient to bring the total volume added to about 25 ml. Aspirate

[8] J. Ind. Eng. Chem., 11, 954–959 (1919).

until the contents of the reaction cylinder are in solution and thoroughly mixed, then discontinue, close the inlet tube with a small piece of rubber tubing and a clamp, and reduce the pressure in the apparatus slightly by sucking out some air in order to guard against any possible escape of bromine at the ground glass stopper. Allow to stand overnight, then aspirate with a rather strong

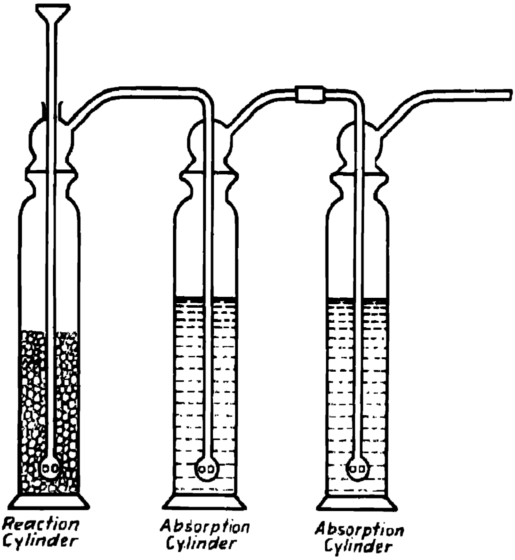


FIG. 18.

current of air (about $\frac{1}{2}$ to $\frac{3}{4}$ l. per min.) for three hours, adding four 2 ml. portions of 3 per cent hydrogen peroxide at thirty minute intervals. Stop the aspiration and evaporate the contents of the two absorption cylinders nearly to dryness. Clean out the reaction cylinder and freshly charge with glass beads and 15 g. chromic anhydride. Into the first absorption cylinder, put 10 g. potassium iodide, dissolved in 200 ml. of water, and into the second 3 or 4 g. in a like amount of water. Connect the apparatus, draw through a slow current of air, and transfer the contents of the evaporating dish to the reaction cylinder by means of a small funnel, using 25 ml. of water. Aspirate with a rather strong current of air until all the bromine is evolved (about 1 hour) and titrate the potassium iodide solution with thiosulfate."

Chromic acid in concentrated solution liberates bromine from bromides quantitatively at room temperature.

Iodides should be removed if present in appreciable amount.

CADMIUM[1]

Cd, *at.wt.* 112.41 *sp.gr.* 8.65; *m.p.* 320.9°; *b.p.* 767° C.; *oxide* CdO

Cadmium occurs in small quantities in practically all zinc ores. It is found in most slab zinc and zinc materials, sheet zinc, zinc oxide, etc. In ores it occurs usually as sulfide, the rare mineral greenockite being CdS. The metal cadmium is largely obtained as a by-product from zinc smelting.

Cadmium is used in alloys. Its alloy with gold is green colored, a popular metal in jewelry; its alloy with silver resists tarnishing. The metal coating is used for rust proofing articles. Added to copper it increases the tensile strength of this metal. It is used in certain alloys as trial plates for silver coinage, and more recently as substitutes for tin base bearing metals. It is used as a paint pigment as the yellow sulfide. It is contained in some dental amalgams.

Cadmium was discovered in zinc carbonate by Stromeyer and simultaneously it was discovered by Hermann in zinc oxide (1817).

DETECTION

The sample is dissolved in aqua regia followed by sulfuric acid, heating until the fumes of H_2SO_4 are strongly evident. The cooled residue is extracted with water and tests made on the extract.

Hydrogen Sulfide Test.—Cadmium is detected in the *wet way* by precipitation as the yellow sulfide by hydrogen sulfide from an acid solution. It is distinguished from arsenic, antimony and tin (stannic) by the insolubility of its sulfide in ammonium hydroxide or colorless ammonium sulfide; from tin (stannous) by its insolubility in yellow ammonium sulfide; and from mercury by its solubility in warm dilute nitric acid. The separation of cadmium may be made from lead since cadmium sulfate is soluble in dilute sulfuric acid while lead sulfate is not; from bismuth since ammonium hydroxide precipitates bismuth hydroxide but holds cadmium in solution, and from copper by passing hydrogen sulfide into the solution containing potassium cyanide which prevents the precipitation of copper sulfide but not cadmium sulfide.

Blowpipe Tests, Dry Methods.—The detection of cadmium may be made in the *dry way* through the tube test. This test is carried out in the following

[1] Original Chapter by L. S. Holstein and L. A. Wilson. Revised for the 5th Edition by L. A. Wilson.

manner. A piece of hard glass tubing of about 5 mm. bore is sealed at one end. From 200–400 milligrams of the fine dried ore is mixed with a reducing agent as dry powdered charcoal and introduced into the tube.[2] The tube is heated just above the mixture of ore and reducing agent and drawn out to a capillary of about 1 mm. diameter. The end of the tube containing the mixture is now heated in the blast lamp and the cadmium together with zinc, arsenic, antimony, etc., is volatilized and condensed in the capillary in the form of separated rings. The cadmium ring is detected from the others by introducing a little powdered sulfur into the tube and heating so that the sulfur vapor passes over the rings. The cadmium is converted to sulfide and appears red while hot and yellow while cold. Very small amounts of cadmium may be detected in this way and it is possible with experience to estimate, from the appearance of the ring, either metallic or sulfide the amount of cadmium present. See Fig. 19.

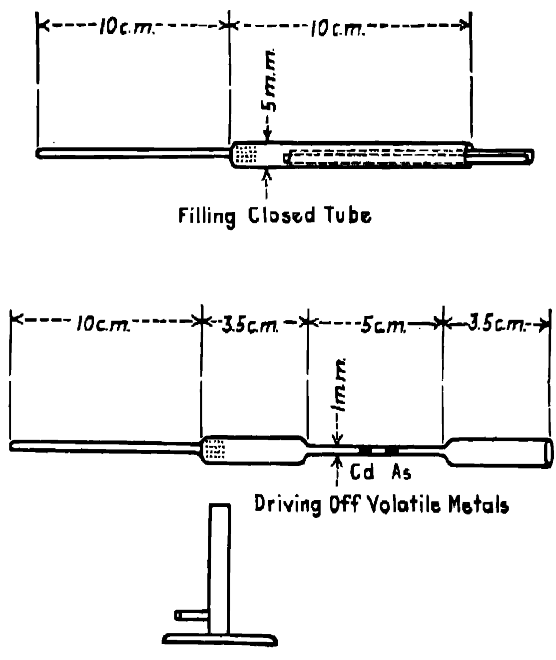


Fig. 19.

Heated on charcoal in the reducing flame, cadmium gives a brown incrustation which is volatile.

Spectrum.—The characteristic lines of cadmium are a red line (6438.49A), a green line (5085.92A) and a blue line (4799.96A) in the visible portion of the spectral range.

[2] All metals present in the ore must be in the oxidized state. Sulfide ores must be carefully roasted before using in this test. In the case of metallic substances, however, no reducing agent is necessary.

ESTIMATION

The determination of cadmium is required in slab zinc sold under specified rejection limits, and in ores to be smelted for slab zinc. It is determined in zinciferous materials where cadmium is deleterious to the finished product.

It is determined in ores, especially zinc bearing in which it commonly occurs, in alloys, paint pigments, and amalgams.

PREPARATION AND SOLUTION OF THE SAMPLE

Samples of metals, as slab zinc, cadmium metal, brass, etc., should be in the form of drillings, sawings or pourings, taken in a proper manner to be representative of the lot and of sufficient fineness to preclude a nonrepresentative sample being weighed for analysis. The samples of ore or fine material should be ground to pass a 100-mesh screen. Metallics, if also present, are kept separate from the fine material which passes through the screen, and in weighing out the sample, proportional amounts of each are taken.

Metallic cadmium is slowly soluble in hot, moderately dilute hydrochloric acid and in hot dilute sulfuric acid. It is readily soluble in nitric acid. The oxide of cadmium is soluble in mineral acids.

Ores.—Decomposition is best effected by the action of hydrochloric acid, followed later by nitric acid, or by the immediate treatment with aqua regia. When the action has subsided sulfuric acid is added and the solution taken to fumes. The cooled solution is now extracted with water and filtered from the silica and lead sulfate residue.

Carbonates are best decomposed with hydrochloric acid.

Alloys, Slab Zinc, Amalgams.—These are decomposed by action of hydrochloric acid, aqua regia, followed by sulfuric acid and expulsion of HNO_3 (and HCl) by taking to strong white fumes of H_2SO_4.

Paint Pigments.—See chapter on Paint.

SEPARATIONS

Cadmium may be determined after separation from other elements by weighing the CdS, the accuracy of which has been questioned; [3] by converting the sulfide to sulfate and weighing; as the metal following electrolysis or volumetrically by titration with iodine of the H_2S liberated from CdS.

Removal of Silica.—Evaporate with hydrochloric acid or sulfuric acid and filter off the dehydrated silica, using suction.

Removal of Lead.—Evaporate to fumes with sulfuric acid, cool, take up with water, warm until all soluble salts are dissolved and allow to stand until all lead sulfate settles. By using sulfuric acid to dehydrate the silica, lead and silica may be separated together.

Separation from Ammonium Sulfide Group (Except Zn), Alkaline Earths and Alkalies.—The solution from lead and silica separation containing 12 ml. sulfuric acid (1 : 1) per 100 ml. of solution is saturated cold with hydrogen sulfide, passing a steady stream for twenty to thirty minutes, and after the first

[3] See p. 201.

five minutes adding a drop of ammonium hydroxide and continuing until zinc sulfide precipitates in quantity. It is necessary to add ammonium hydroxide to bring down zinc in order to assure the complete precipitation of cadmium. The precipitate of sulfides is filtered off and washed with cold water.

Removal of Arsenic, Antimony and Tin.—The precipitate on the filter is washed with ammonium hydroxide or colorless ammonium sulfide, dissolving out the arsenic, antimony and tin (stannic). If tin in the stannous condition is found to be present, yellow ammonium sulfide must be used. This treatment is not always necessary since arsenious sulfide is practically insoluble in the hydrochloric acid of the concentration (1 : 2) used in dissolving the cadmium sulfide. Antimonious sulfide is also only slightly soluble, so that these sulfides remain behind in carrying out the analysis.

Tin may be removed with the bismuth by precipitation with ammonium hydroxide as described in the following.

Removal of Bismuth, Copper and Mercury.—Bismuth is not removed in the course of analysis as its sulfide is soluble in hydrochloric acid and hence it must be removed by precipitating with ammonium hydroxide before the final precipitation of cadmium is made. Copper sulfide is, however, practically insoluble in the hydrochloric acid used and remains behind when dissolving the first precipitates of cadmium sulfide. Mercuric sulfide is practically insoluble in cold hydrochloric acid (1 : 2) and is left behind in carrying out the analysis.

Separation from Zinc.—Cadmium is separated from the accompanying zinc by successive precipitations with hydrogen sulfide, each time bringing down less zinc, until finally only cadmium is precipitated. In the presence of a large quantity of zinc it is not possible to precipitate all cadmium with the acidity required to prevent the precipitation of any zinc sulfide.

See further details for the separation of cadmium under Gravimetric Methods.

GRAVIMETRIC METHODS

SEPARATION OF CADMIUM AS CADMIUM SULFIDE

A 10 gram sample of the finely pulverized ore is weighed out into a 400-ml. beaker, moistened with water and 50 ml. of aqua regia carefully added.[4] When violent action has stopped, the beaker is placed on a warm plate to complete decomposition. The cover glass and sides of beaker are washed down with

[4] This procedure is also applicable for slab zinc, alloys, etc. A 10-gram sample is suitable for materials containing about 0.1% to 1.0% Cd. It is necessary when other amounts of samples are taken to vary the quantity of sulfuric acid so that approximately 7% of free acid is present before precipitating.

water, 25 ml. of sulfuric acid (1 : 1) added and evaporation carried to fumes. Water (100 ml.) is added, boiled until all soluble salts are dissolved, and the residue filtered off, and washed, using suction.

A steady stream of hydrogen sulfide is passed through the filtrate, which should have a volume of approximately 300 ml., for thirty to forty minutes. After all iron in solution has been reduced, ammonium hydroxide is added 1 ml. at a time until a heavy precipitation of zinc sulfide has taken place.[5] The precipitate is allowed to settle, the clear solution decanted and finally the bulk of the precipitate transferred to a 15-cm. paper, and washed with cold water. The sulfides on the paper are dissolved with hydrochloric acid (1 : 2) catching the solution in a clean beaker. Any precipitate adhering to the sides of the original beaker is also dissolved off and poured into the filter. After all zinc sulfide has been dissolved, the paper is washed three more times with the hydrochloric acid.[6] To the solution 15 ml. of sulfuric acid (1 : 1) is added and evaporation carried just to fumes. Water is added (200 ml.) and hydrogen sulfide passed through as before. Ammonium hydroxide should be added one drop at a time, only to start the precipitation of cadmium sulfide. This precipitate is filtered off, redissolved as previously and a third precipitation made.[7] Before making the final precipitation, the solution should be allowed to stand, and any lead sulfate filtered off. The final precipitate of cadmium sulfide is filtered on a weighed Gooch crucible. After drying at 110° C. for one hour, the crucible is cooled, reweighed and the cadmium calculated from the difference in weights [8]

$$CdS \times .778 = Cd.$$

The cadmium sulfide need only be washed once or twice, as it usually receives sufficient washing in the transfer to the filter, and in the scrubbing and washing out of the beaker.

NOTES.—It is seldom that bismuth and tin will be encountered in making a determination for cadmium so that the procedure for removing these elements need rarely be used. Cadmium sulfide precipitated from sulfuric acid is bright yellow to orange. If the precipitate is brown in color, bismuth and tin should be looked for and removed.

DETERMINATION OF CADMIUM AS CADMIUM SULFATE

Cadmium separated from other elements as CdS may now be converted to $CdSO_4$ and so determined.

[5] The solution should always be sufficiently acid so that no iron, etc., precipitates.

[6] This strength of acid will leave on the paper as an insoluble residue all the As, Cu, and Hg, most of the Sb, and some of the Bi and Sn. The second precipitation of CdS should free the Cd of the rest of the Sb, but not the Bi or Sn.

[7] It is necessary to make three or even four precipitations of cadmium sulfide in order to free it completely of zinc. The filtrates may be readily tested for zinc by adding a few drops of a 10% solution of potassium ferrocyanide. Not more than a slight turbidity should be present in the filtrate from the final precipitation.

[8] Results will be slightly high—approximately 3%—because the composition of the precipitate is not exactly CdS. Where greater accuracy is desired weighing the cadmium as cadmium sulfate or an electrolytic determination of the cadmium is recommended.

The final precipitate of cadmium sulfide is dissolved with hydrochloric acid, and evaporated to dryness in a weighed platinum crucible or dish. A slight excess of dilute sulfuric acid is poured over the residue and evaporated over a steam bath or warm plate. The excess of sulfuric acid is driven off by heating in an air bath, or in a muffle heated below a dull red heat. For an air bath, the crucible or dish may be placed in a larger vessel, and this outer vessel heated to redness. $CdSO_4 \times 0.5392 = Cd$.

ELECTROLYTIC DETERMINATION OF CADMIUM

The final precipitate of CdS is dissolved and the cadmium determined electrolytically as given under cadmium in slab zinc, Chapter on Zinc, or if the amount of cadmium is large the electrolytic determination is best carried out with a potassium cyanide electrolyte. The hydrochloric acid solution of cadmium, after separation of interfering elements is taken to fumes with sulfuric acid, a drop of phenolphthalein added for indicator, and a pure solution of sodium hydroxide added until a permanent red color is obtained. A strong solution of potassium cyanide is added drop by drop until the cadmium hydroxide just dissolves, avoiding any excess. The solution is diluted to 100 ml. with water, electrolyzed cold using a gauze electrode with a current of 0.5–0.7 ampere and voltage of 4.8–5.0. At the end of five to six hours the current is increased to 1–1.2 amperes and electrolysis continued for an hour more. The electrode is removed from the solution the instant the current is broken and immediately washed with water, followed by alcohol and ether. After drying at 100° C., the electrode is cooled and weighed. Prolonged heating of the deposit should be avoided.

Rapid deposition can be effected by means of the rotating anode (600 revolutions per minute). The solution of cadmium sulfate containing 3 ml. of H_2SO_4 (1 : 10) per 150 ml., heated to boiling, is electrolyzed with a current of $N.D._{100} = 5$ amperes, E.M.F. = 8–9 volts. Fifteen minutes is sufficient for the deposition of .5 gram of cadmium.[9]

NOTES.—Before washing and discontinuing the current, it is advisable to add a little water to raise the level of the liquid and continue the electrolysis to ascertain whether the deposition is complete.

Traces of cadmium may be estimated in the above solution by saturating this with H_2S and comparing the yellow-colored colloidal cadmium sulfide solution with a known quantity of cadmium and the same amounts of potassium hydroxide and cyanide as in the solution tested.

[9] Electro Analysis, E. F. Smith. P. Blakiston's Son & Co. Phila. Pa.

VOLUMETRIC DETERMINATION OF CADMIUM

TITRATION OF CADMIUM SULFIDE WITH IODINE[10]

The method is applicable to the determination of from 10 mg. to 200 mg. or more, and depends upon the following reaction:

$$CdS + 2HCl + 2I = CdCl_2 + 2HI + S.$$

Low results are apt to be obtained—as much as 8% for 0.2 g. Cd and 4% for 0.05 g.—because the precipitate is not pure CdS but contains some of the cadmium in the form of the sulfate.

Procedure.—The amount of the sample taken should be such that the cadmium content is between 10 mg. to 200 mg. and the material is treated as outlined in the gravimetric method, p. 200.

The precipitate of CdS is washed and allowed to drain on the filter. The filter, together with the sulfide, is placed in a beaker or an Erlenmeyer flask, water added, and the whole shaken to break up the precipitate. A moderate quantity of hydrochloric acid is added and the solution titrated with standard N/5 or N/10 iodine solution. Towards the end a little starch solution is added and the titration continued until the excess of iodine colors the solution blue. If preferred, an excess of iodine solution may be added and the excess determined by a back-titration with standard thiosulfate solution.

One ml. N/10 iodine = 0.00562 gram cadmium.

Other Volumetric Methods.—Cadmium is precipitated quantitatively by sodium anthranilate from a neutral solution. Zinc, nickel, copper and cobalt form similar precipitates under the same conditions, but the alkali and alkaline earth ions are not precipitated.[11] The precipitate may be weighed, or it may be dissolved and titrated by the bromate-bromide excess method.[12]

Cadmium pyridine thiocyanate may be precipitated, filtered and the excess of thiocyanate titrated with standard silver nitrate.[13]

DETERMINATION OF CADMIUM IN METALLIC CADMIUM

Details of the method are essentially those given by Robert Keefer, Late Chief Chemist, Anaconda Copper Company, in his work, Methods in Non-Ferrous Metallurgical Analysis.[14]

Solution of the Metal.—One gram of the metal is dissolved in a 400-ml. beaker, after addition of a few ml. of water, by 10 to 15 ml. of HNO_3 and warming gently. Ten ml. of H_2SO_4 are now added and the solution evaporated to strong fumes, using care to prevent splattering. After cooling, 100 ml. of

[10] P. von Berg (Z. anal. Chem., **26**, 23 (1887)) transfers the precipitate and filter to a stoppered flask, expels the air with CO_2 and by boiling and then titrates in an hydrochloric acid solution. Experiments by the author have shown this caution to be unnecessary.

[11] Funk and Ditt, Z. anal. Chem., **91**, 332 (1933).

[12] Shennan, Smith and Ward, Analyst, **61**, 395 (1936).

[13] Spacu and Kuras, Z. anal. Chem., **99**, 26 (1934).

[14] McGraw-Hill Book Co.

water are added and the solution heated to boiling, then cooled and filtered if a precipitate ($PbSO_4$) is present.

The filtrate is carefully neutralized by addition of dilute NH_4OH (litmus indicator) and diluted to 250 ml. Five ml. of concentrated H_2SO_4 are added and the solution saturated with H_2S (30 minutes). The sulfide is filtered off and the filtrate tested for zinc by addition of NH_4OH. If much zinc is evident by the cloudy precipitate forming (ZnS) it is advisable to repeat the precipitation of CdS to eliminate the ZnS occluded. The precipitate on the filter is dissolved in warm HCl (1 : 1) and the precipitation of CdS repeated according to the directions above.

The purified sulfide is dissolved in hot HCl (1 : 1) in the original beaker in which the precipitation was made. Twenty to 25 ml. of concentrated H_2SO_4 are added and the solution evaporated to small bulk on the steam bath, then on a hot plate to near dryness. After cooling 20 ml. of water are added, the sulfate brought into solution by warming and the solution transferred to a weighed porcelain crucible. The rinsings of the beaker are placed in a second weighed crucible. The solutions in both crucibles are evaporated to dryness on a steam plate.

The residues are heated to expel free sulfuric acid and then ignited in a muffle below a red heat and the sulfates weighed. The results are excellent, a high degree of accuracy being obtained.

CALCIUM

Ca, ***at.wt.*** **40.08;** ***sp.gr.*** **$1.5446^{20°}$;** ***m.p.*** **810° C.;** ***oxide,*** **CaO**

This exceedingly important and widely distributed element occurs in nature only in combined state. It is estimated that calcium forms 3.5 per cent of the earth's crust. It occurs combined as carbonate, sulfate, phosphate, fluoride, silicate and in a large number of complex compounds associated with a number of elements, among which are silicon, iron, aluminum, boron, titanium, sodium and potassium. Among the better known minerals are calcite, limestone, iceland spar, carbonates of calcium; dolomite, calcium and magnesium carbonate; anhydrite and gypsum, calcium sulfate; fluorite or fluor spar, calcium fluoride; apatite, a complex compound of calcium fluoride and phosphate. Calcium is found in nearly all mineral springs, artesian and river water, principally as bicarbonate. As oxalate it occurs in plants; as phosphate in bones of animals. It is an essential constituent of many rock forming minerals.

DETECTION

In the usual course of qualitative and quantitative analysis calcium passes into the filtrates from the elements precipitated by hydrogen sulfide in acid and alkaline solutions (Ag, Hg′, Hg″, Pb, Cu, Cd, As, Sb, Sn, Fe, Cr, Al, Mn, Ni, Co, Zn, etc.), and is precipitated from an ammoniacal solution by ammonium carbonate as calcium carbonate, along with the carbonates of barium and strontium. The separation of calcium from barium and strontium is considered under Separations. The oxalate of calcium is the least soluble of the alkaline-earth group. All, however, are soluble in mineral acids. Calcium oxalate may be precipitated from weak acetic acid solution by ammonium oxalate, or from neutral solutions by oxalic acid, as a colorless crystalline compound, $CaC_2O_4 \cdot H_2O$.

Flame Test.—The flame of a Bunsen burner is colored yellowish red when a platinum wire containing calcium salt moistened with concentrated hydrochloric acid is held in the flame.

Spectrum.—An intense orange and green line with a less distinct violet line. Note chart of the spectra of the alkaline earths. Plate II.

See also the chapter on Barium under Separations—Preliminary Tests.

Calcium oxide or lime has been known for many centuries. It was for a long period considered to be an elementary substance. Davy believed the substance to be made up of an oxide and a metal, but was not successful in his attempt to obtain the pure element, but paved the way to its isolation by electrolysis of the chloride.

Although the element calcium has not found any commercial use its compounds are exceedingly important. Lime is an important constituent of cement, lime stucco, and plaster. Its numerous uses in the industries in building materials, in pharmaceutical preparations, in insecticides, in the beet sugar industry, in tanning, in the dairy in butter-making, in the paper industry, etc. are well known.

ESTIMATION

In practically all complete analyses of rocks, minerals, soils, water the determination of calcium is necessary. Its estimation is required in the analysis of mortar, cement, bleaching powder, plaster of Paris, certain paint pigments, phosphorescent paint (CaS), plant ash, certain fertilizers, etc.

In analytical procedures of separations it should be kept in mind that the sulfates of the alkaline earths are difficultly soluble, so that in presence of sulfates, combined barium, calcium and strontium are apt to remain, wholly or in part with the silica residue, and must be recovered here. If fluorine has not been expelled in the preliminary treatment, calcium will precipitate with iron and aluminum when ammonia is added, CaF_2 being insoluble in ammoniacal solutions. If phosphates are present and iron is not present in sufficient amount to take care of PO_4, calcium will precipitate with the ammonium sulfide group when the solution is made ammoniacal, causing an error in the aluminum determination as well as that of calcium.

The alkaline earths are best converted to chlorides by the action of HCl on their ores. The silica residue remaining from the acid extraction is fused with Na_2CO_3, extracted with water to remove sodium silicate and the carbonate residue dissolved in HCl. Calcium will be found in the hydrochloric acid solutions.

PREPARATION AND SOLUTION OF THE SAMPLE

The oxide, hydroxide, carbonate, phosphate, and fluoride of calcium are soluble in hydrochloric or nitric acids. The sulfates (gypsum, anhydrite, etc.), certain silicates and complex compounds require fusion with Na_2CO_3 followed by solution in water and hydrochloric acid. Characteristic substances will be considered. Special products will receive attention later.

Decomposition of Material.—Though carbonates are easily dissolved in hydrochloric acid, sulfates and fluorides of calcium require fusion with sodium

and potassium carbonate to effect decomposition. In case calcium fluoride is being decomposed, the addition of an equal weight or more of silica is necessary, and sodium or potassium hydroxide may be substituted for potassium carbonate. The fusion is leached with water to remove the mineral acids, and the residue, containing all of the calcium, is dissolved in hydrochloric acid. Calcium is now determined in the hydrochloric acid solution. If phosphate is present in the sample, it is not completely removed by the water leaching as sodium phosphate, as this reacts in the solution with calcium carbonate causing a partial conversion to calcium phosphate, which remains in the residue. In this case it is advisable to precipitate calcium oxalate by addition of ammonium oxalate from a slightly acid solution, in which calcium phosphate will not precipitate, as it would if the solution was made ammoniacal.

Solution of Limestones, Dolomites, Magnesites, Cements, Lime, etc.—One gram of the powdered material is digested in a 250-ml. beaker with 20 ml. of water, 5 ml. of concentrated hydrochloric acid, and 2 or 3 drops of nitric acid (sp.gr. 1.42). The beaker is covered to prevent loss by effervescence. When the violent action has subsided, the sample is placed on a hot plate and boiled for a few minutes. The watch-glass is rinsed into the beaker and the solution filtered. The residue is washed, dried and ignited in a platinum crucible, and then fused with a little sodium carbonate or bicarbonate. The cooled fusion is dissolved in hot dilute hydrochloric acid, the liquid added to the main solution and calcium determined by precipitation as calcium oxalate, after removal of silica, iron, alumina, etc.

In presence of sulfates it may be advisable to leach out the silica before dissolving the water insoluble carbonates containing the alkaline earths.

Silicates.—Solution of silicates is best obtained by direct fusion of 1 gram of the powdered material with 4 to 5 grams of sodium carbonate, in a platinum crucible. The cooled melt is now covered with water and dissolved with hydrochloric acid according to the standard procedure for carbonate fusions. The hydrochloric acid solutions are taken to dryness and the silica dehydrated in an oven at 110° C. for an hour and then the residue is extracted with dilute hydrochloric acid and filtered. The filtrate contains iron, alumina, magnesium, lime, etc.

In presence of sulfates and the alkaline earths it will be necessary to remove sodium silicate by extraction with water, before treating the water insoluble carbonates of this group with acid. This must be born in mind in all separations of silica from this group.

Solution of Gypsum, Plaster of Paris, and Sulfates of Lime, etc.—The treatment of the sample is similar to the one given above with the exception that it is advisable to add a larger amount of concentrated hydrochloric acid, e.g., about 20 to 25 ml. If barium sulfate is present it is indicated by the clouding of the solution upon acidifying the water extract of the carbonate fusion.

Chlorides, Nitrates, and Other Water-soluble Salts.—These are dissolved in water slightly acidified with hydrochloric acid.

Sulfides, Pyrites Ore, etc.—The ore should be oxidized with bromine or by roasting, previous to the acid treatment.

SEPARATIONS

The solution for calcium determination should be free from silica, sulfur, phosphates, fluorides and carbonates and from the hydrogen sulfide and ammonium sulfide group elements.

Removal of Silica.—The acid solution obtained by the decomposition of the ore is evaporated to dryness and baked at 110° C. to dehydrate SiO_2. The residue is moistened with HCl and water added. After heating to near boiling the solution is filtered from the impure SiO_2. The residue is washed with water containing HCl (1 : 100). The filtrate is set aside for the calcium determination.[1]

In presence of sulfate calcium is apt to be left in part with the silica. It may be recovered by fusion of the residue with Na_2CO_3 leaching out the sodium silicate (and sulfate), dissolving the water insoluble carbonate with HCl and again evaporating to separate any occluded silica. The residue is again extracted with HCl and water and filtered. The combined filtrates and washings containing calcium are further treated to remove substances interfering with the calcium determination.

Removal of Copper, Nickel, Cobalt, Manganese, Zinc and Other Elements Precipitated by H_2S in Acid and Alkaline Solutions.—This separation is seldom required in lime-bearing ores. In the analysis of pyrites, and ores commonly containing the above elements this separation should be made.

The solution obtained after separation of silica is made slightly ammoniacal (See notes below) and saturated with H_2S, and filtered. If arsenic, antimony and tin are present, precipitation is first carried out in acid solution and filtered and the filtrate made alkaline and again saturated with H_2S and filtered. The details are carried out according to the well known standard procedures used in removing the H_2S and $(NH_4)_2S$ groups. Calcium is in the filtrate.

Notes.—Should phosphates be present in excess of the amount that would be removed by iron and alumina, calcium will precipitate as phosphate when the solution is made ammoniacal. Provision should be made for its recovery, if this is the case.

Fluoride should be absent for in their presence CaF_2 precipitates here also.

The ammonium hydroxide should be free from carbonate, whose presence would cause the precipitation of $CaCO_3$.

Removal of Fluoride.—The presence of the fluoride ion will cause the precipitation of CaF_2 during the procedure for removal of iron and aluminum, since CaF_2 is insoluble in ammoniacal solution. Fluorine is removed in the initial decomposition of the ore. Sufficient silica should be present to form silicon fluoride which is expelled by taking to fumes with H_2SO_4. It may be necessary to add a few milligrams of fine, pure silica (A. A. Noyes, Tech. Quarterly, **16**, 101, 1903).

Removal of Phosphate.—If phosphate ion is present in excess of that which the iron in the solution will precipitate, it may be removed by adding an excess of iron,[2] or by precipitation with ammonium molybdate (free from calcium). Molybdenum does not interfere in the precipitation of calcium as oxalate. Consult the chapter on Phosphorus.

[1] The perchloric acid procedure is excellent for the separation of the silica. See Chapter on Silicon.

[2] For example in presence of 0.005 g. P_2O_5 and 0.05 g. CaO, a tenfold excess of iron or aluminum, i.e. 0.03 g. Fe or Al, is used.

Removal of Iron and Aluminum.—The removal of iron and aluminum is generally necessary in the analysis of natural substances carrying calcium. In absence of fluoride, phosphate and carbonate ions the iron and aluminum may be precipitated with ammonium hydroxide added in amount sufficient to turn methyl orange indicator yellow, avoiding an excess that would dissolve aluminum hydroxide. (Consult the chapter on Aluminum.) The precipitate is filtered off, saving the filtrate for calcium. The hydroxides are dissolved in HCl and the filtrate, diluted with the washings of the filter, again treated with NH_4OH, added drop by drop to complete precipitation of iron and aluminum. The precipitate is again filtered and the two filtrates combined for the determination of calcium.

NOTE.—Good results have been obtained by precipitation of calcium oxalate from an acid solution in presence of iron and aluminum. Separation may be effected from iron, aluminum, titanium, zirconium, phosphate ion, barium and magnesium. The outline of the procedure is as follows:

Precipitation of Calcium Oxalate in Presence of Iron and Aluminum, etc.—The solution containing the phosphates freed from silica is oxidized by boiling with nitric acid as usual. Ammonia water is added to the cooled solution until a slight precipitate forms, and then citric acid is added in sufficient quantity to just dissolve the precipitate. If this does not readily occur, additional ammonia is added, followed by citric acid until the solution clears, then about 15 ml. of citric acid in excess. The solution is diluted to 200 ml. and heated to boiling. Calcium oxalate is now precipitated by addition of ammonium oxalate. Iron and alumina remain in solution.

Citric acid is made by dissolving 70 grams of the acid, $H_3C_6H_5O_7 \cdot H_2O$, in a liter of water.

Wagner's Solution.—In place of citric acid, the following solution may be used. Twenty-five grams of citric acid and 1 gram of salicylic acid are dissolved in water and made to 1000 ml. Twenty-five to 50 ml. of this reagent is effective in preventing precipitation of iron and alumina.

An excellent separation of calcium from iron, aluminum, titanium, zirconium and large amounts of phosphorus may be made by precipitation of calcium oxalate from neutral solution by means of oxalic acid followed by ammonium oxalate. In a double precipitation, barium and magnesium do not interfere. Details are given under the gravimetric methods for determining calcium.

Separation of Calcium from the Alkaline Earths, Barium and Strontium and from Magnesium.—The separations have been discussed in the chapter on Barium. A brief outline follows:

Separation of Calcium from Barium and from Strontium.—The alkaline earths are converted to nitrates, all moisture expelled by heat, and calcium nitrate extracted from the insoluble nitrates of barium and strontium by a mixture of anhydrous ether and absolute alcohol, in equal parts, or by boiling the dry nitrates in amyl alcohol (*b.p.*, 137.8° C.). Details of the procedure are given under Separations of the Alkaline Earths in the chapter on Barium.[3]

Separation of Calcium from Magnesium and the Alkalies.—In the presence of considerable amounts of calcium and comparatively small quantities of magnesium the oxalate method of precipitating calcium, in presence of ammonium chloride, is generally sufficient for precipitating calcium free from

[3] 100 ml. dissolves 37 grams of Ca $(NO_3)_2$ and only 0.001 g. Sr $(NO_3)_2$.

magnesium and the alkalies. In analysis of dolomite, $MgCO_3 \cdot CaCO_3$, and of samples containing comparatively large amounts of magnesium, a double precipitation of calcium is generally necessary for removal of occluded magnesium.

GRAVIMETRIC DETERMINATION OF CALCIUM

PRECIPITATION OF CALCIUM OXALATE AND IGNITION TO CALCIUM OXIDE

The solution of calcium free from interfering elements is treated as follows:—Calcium oxalate is precipitated from feebly ammoniacal solutions or from solutions acidified with acetic, oxalic, citric, salicylic or o-phthalic acids, by means of ammonium oxalate. The presence of ammonium chloride hinders precipitation of magnesium and does not interfere with that of calcium. If, however, much magnesium (or sodium) is present it will contaminate the calcium precipitate so that a second precipitation is necessary to obtain a pure product. The compound formed from hot solutions is crystalline or granular and filters readily, whereas the flocculent precipitate formed in cold solutions does not. Calcium oxalate, $CaC_2O_4 \cdot H_2O$,[4] decomposes at red heat to CaO, in which form it is weighed.

Procedure.—If the calcium determined is in the filtrate from previous groups, hydrogen sulfide is expelled by boiling and the precipitated sulfur filtered off, the solution having been concentrated to about 100 ml. The filtrate should contain sufficient ammonium chloride to hold magnesium in solution in presence of ammonium oxalate (i.e., about 10 grams NH_4Cl per 0.0015 gram MgO per 100 ml. of solution). If not already present, the chloride is added in sufficient amount, and the solution diluted to about 150 ml. Generally sufficient NH_4Cl is obtained by adding 10 ml. HCl (sp.gr. 1.2) and neutralizing with NH_4OH. The solution is now acidified with a weak organic acid, oxalic acid preferred, and 10 ml. added in excess (10% soln.) to the hot solution, stirring vigorously. Now about 150 ml. of a saturated solution of ammonium oxalate (4% soln.) are added in a fine stream with vigorous stirring. The precipitate is settled on a steam bath for an hour or more and is filtered. The calcium oxalate is washed with water containing oxalic acid and ammonium oxalate (1 g. oxalic acid or 2 g. ammonium oxalate per liter).[5]

[4] Calcium oxalate dried at 100° C. = $CaC_2O_4 . H_2O$. Heated to 200° C. = CaC_2O_4. At 550° C. the oxalate begins to decompose, free carbon is liberated, and calcium carbonate begins to form. At bright red heat carbon burns off and the carbonate is completely decomposed to the oxide and CO_2.

[5] Acidity should not exceed pH 4, according to A. T. School (J. Biol. Chem., 50, 527–36, 1922.

H. D. Chapman (Soil Sci., 26, 479–86, 1928) recommends a pH of 4 for Ca in soils. Fe, Al, Ti, Mn, Mg, P_2O_5 do not interfere. CaC_2O_4 precipitates at this acidity.

If considerable magnesium is present a double precipitation should be made. The washed precipitate is dissolved in about 50 ml. of dilute HCl (1 : 4) and calcium oxalate reprecipitated as in the first procedure, by neutralizing HCl with NH_4OH and adding a small amount of oxalic acid and ammonium oxalate and again filtering and washing.

The filter is placed in a weighed crucible and gently heated, the crucible being covered, until the water is expelled and the paper charred. The heat is increased to the full temperature of the burner (1200° C.) and the heating continued for 5 to 10 minutes. It is well to remove the cover for an instant to assist escape of the CO_2 during the blasting. The covered crucible and its contents are cooled in a desiccator containing conc. sulfuric acid. The cooled CaO is weighed and the ignition repeated until the weight is constant. If a platinum crucible is used constant weight is rapidly attained. A longer period is required when porcelain is used. The Tirrill, Meker or Teclu burners give satisfactory results.

Weighing should be done quickly as CaO absorbs moisture from the air.

Factors. $CaO \times 0.7147 = Ca$, or $\times 1.7847 = CaCO_3$, or $\times 2.8908 = Ca(HCO_3)_2$, or $\times 2.4276 = CaSO_4$.

WEIGHING OF CALCIUM AS CALCIUM CARBONATE [6]

The recommended procedure for the determination of calcium (in solutions of its pure salts) is as follows. Precipitate the oxalate by adding to the hot acid solution twice the theoretical amount of ammonium oxalate (or oxalic acid), and slowly neutralize with 1 : 5 ammonium hydroxide, using methyl red as indicator. Let the solution stand on the hot-plate for two hours, filter through a filtering crucible (or a Gooch), dry at 110° for thirty minutes and ignite in an electric muffle for one hour at a temperature between 475 and 500°. For the separation of calcium from other elements the usual methods are applicable, followed by ignition to carbonate as above.

VOLUMETRIC DETERMINATION OF CALCIUM

TITRATION OF THE OXALATE WITH PERMANGANATE

This procedure may be applied successfully in a great variety of instances on account of the readiness with which calcium oxalate may be separated. In the presence of iron, alumina, manganese, magnesia, etc., it is advisable to make a reprecipitation of calcium oxalate to free it from adhering contaminations.

[6] Willard and Boldyreff, J. Am. Chem. Soc. 52, 1888 (1930).

The following reaction takes place when potassium permanganate is added to calcium oxalate in acid solution:

$$5CaC_2O_4+2KMnO_4+8H_2SO_4=5CaSO_4+K_2SO_4+2MnSO_4+10CO_2+8H_2O.$$

Procedure.*—Calcium oxalate, obtained pure, by precipitation and washing according to directions given under the gravimetric determination of calcium, is washed into a flask through a perforation made in the filter paper, the filter is treated with a little warm, dilute sulfuric acid and the adhering oxalate dissolved and washed into the flask. About 25 ml. of dilute sulfuric acid, 1 : 1, is added and the solution diluted to 250 to 300 ml.

When the precipitate has dissolved, the solution is titrated with standard potassium permanganate under the conditions described in the Chapter on Standard Solutions.

One ml. N/10 $KMnO_4$ = 0.002004 gram Ca, or $\times$0.002804 = CaO.

Factors. Ca$\times$1.3992 = CaO or $\times$2.4970 = $CaCO_3$ or $\times$3.3967 = $CaSO_4$ or $\times$2.5805 = $Ca_3(PO_4)_2$.

NOTES. **Precipitation from Acetic Acid Solution.**—This is recommended if the material contained phosphates. The solution should contain about 1 ml. free glacial acetic acid per two hundred ml. of solution. In presence of phosphate, iron and aluminum cannot be removed by addition of ammonia as calcium would also precipitate as phosphate. Citric or oxalic acid may also be used to prevent precipitation of iron.

Procedure.—To a volume of about 75 ml. of solution containing 0.1 to 0.15 g. Ca add 10 ml. acetic acid (glacial), heat to boiling and add slowly 10 ml. of a saturated solution of ammonium oxalate. Now add a slight excess of ammonia and make slightly acid with acetic acid (about 0.5 ml. per 100 ml. solution). If phosphate is present this last acidification is necessary, likewise in presence of aluminum.

"Micro-photographs indicate that better crystals are formed by precipitation from acetic acid solutions than from NH_4OH solutions. The following procedure is recommended. To a water solution of .1–1.5 g. Ca in 75 ml. add 10 ml. concentrated acetic acid, heat to boiling and add slowly from a burrette 7–10 ml. of a cold saturated solution of $(NH_4)_2C_2O_4$ at the rate of 1 drop in 5 seconds. Finally add a slight excess of NH_4OH." A. H. Erdenbrecher, Mikrocosmos, **16**, 201–2, 1923 (C. A., **17**, 3462).

Phosphate ion should be absent or taken care of in the precipitation of calcium. Manganese may be removed by treating the solution with NH_4OH, bromine chlorides being absent. See chapter on Manganese.

AVAILABLE LIME

This is the usual method followed in cyanide mills for determining the per cent which will dissolve the lime added to the mill solution, and therefore the amount to add to maintain the desired protective alkalinity.

Procedure.—One gram of the finely ground sample is placed in a glass stoppered bottle which has been previously marked to hold 500 ml. Thirty grams of sugar and about 300 ml. of water are added and the bottle shaken vigorously. The solution is diluted to 500 ml. and shaken at ten minute intervals for 1½ to 2 hours. Then the insoluble material is allowed to settle, part of the solution filtered through a coarse filter paper, 50 ml. of the filtrate drawn out with a pipette into an Erlenmeyer flask, two drops of phenolphthalein indicator added, and the solution titrated with N/10 oxalic acid solution till the pink color disappears. The lime is reported as per cent available CaO.

1 ml. N/10 Oxalic Acid = .0028 grams CaO.

Standard N/10 Oxalic Acid Solution.—Dissolve 6.303 grams $H_2C_2O_4 . 2H_2O$ in distilled water and dilute to 1000 ml. The solution ordinarily need not be standardized as the weight of the oxalic acid is constant.

To standardize, take 30 ml. of the solution, add 100 ml. of water and 5 ml. of conc. H_2SO_4, heat to 70° C. and titrate to a permanent pink with N/10 $KMnO_4$.

* The calcium oxalate must be washed free of ammonium oxalate, using distilled water in the final washing.

RAPID IODINE METHOD FOR CALCIUM OXIDE IN PRESENCE OF CALCIUM CARBONATE

The method worked out by John C. Bailar, Great Western Sugar Company, is based on the fact that a solution of iodine reacts with calcium hydroxide, but does not react with calcium carbonate. The method is used in the evaluation of lime.

Reagents. ***Iodine Solution.***—A standard solution is made by dissolving 90 grams of potassium iodide and 45.27 grams of iodine in the least quantity of water necessary to effect solution, and diluting with water to one liter. 1 ml. is equivalent to 0.01 g. CaO.

Thiosulfate Solution.—The reagent is made by dissolving 44.27 grams of thiosulfate of sodium in water and diluting to one liter. Two ml. of this solution is equivalent to one ml. of the iodine solution.

Standardization.—A definite weight of 0.5 to 1.0 gram of pure arsenious oxide (As_2O_3) is dissolved in 10% sodium hydroxide solution and the resulting product acidified with hydrochloric or sulfuric acid. This solution is now neutralized with sodium bicarbonate and 4 to 5 grams added in excess. Starch indicator is now added and the arsenite titrated with the standard iodine solution. Since one gram of As_2O_3 is equivalent to 0.5670 gram of CaO, the weight of the arsenic taken multiplied by 0.5670, divided by the ml. of iodine required, gives the equivalent lime per ml. of the standard iodine reagent. Use this factor in the iodine titrations of lime.

The thiosulfate may be standardized against a definite volume of the iodine reagent and its equivalent value established in terms of the standard iodine solution. See Notes below.

Procedure.—The sample of lime (one gram is recommended) is slacked by adding boiling water (5 to 10 minutes is ample to accomplish this). An excess of iodine is added (see Notes) and the mixture stirred occasionally until the lime is all in solution. Insoluble silica is generally present but can easily be distinguished from the milky appearing lime. When the solution of the lime is complete (1 to 10 minutes will accomplish this), the excess of iodine is titrated with the standard thiosulfate. The excess thus determined is subtracted from the total iodine added and the equivalent CaO, to the combined iodine, calculated from the CaO factor of iodine.

NOTES.—Any substance which liberates iodine quantitatively from a solution of potassium iodide can be used for the standardization of sodium thiosulfate. Among such substances are potassium permanganate, potassium dichromate, potassium iodate, potassium bi-iodate, metallic copper oxidized to a cupric salt, etc. In using any of the above reagents first acidify the solution of an excess of potassium iodide with hydrochloric acid (strongly acid if dichromate is used, end point in this case is green in place of colorless) and then add the permanganate or dichromate or other reagent desired and titrate the liberated iodine in presence of starch indicator.

An excess of 5 ml. of iodine is recommended in the lime determination. To the same amount of water used in the analysis add 5 ml. of the iodine and use this as a standard for color comparison in running in the necessary excess of iodine in the sample.

STANDARD METHODS OF TESTING GYPSUM AND GYPSUM PRODUCTS

ADOPTED BY A. S. T. M. IN AMENDED FORM, REVISED 1927, 1930, 1933

Free Water.—Not less than 1 lb. of the entire sample as received shall be weighed, spread out in a thin layer in suitable vessel, placed in a drying oven, and dried at 45° C. for 2 hours. It shall then be cooled in an atmosphere free from moisture, and weighed again. The loss of weight corresponds to the free water, and shall be calculated to percentage of sample as received.

The dried sample shall be stored in an air-tight container until used.

Preparation of Sample.—Dry sample as in Section on Free Water, and reduce about 10 g. until it all passes a 100-mesh sieve, using extreme care not to unduly expose the material to the action of moisture or to overheating. The sample shall be kept in an air-tight container until ready for use.

Combined Water.—Place 1 g. of the sample in a covered crucible and dry at 215 to 230° C. to constant weight. Calculate the loss of weight to percentage of sample as received and report as combined water.

Carbon Dioxide.—Place the residue obtained after drying, as described above, in a suitable flask and dissolve it in dilute HCl (not stronger than 1 : 4) in such a way that the gas evolved, after being freed from H_2O vapor by calcium chloride or sulfuric acid, can be collected in either soda lime or caustic potash and weighed. The solution should be boiled for one minute, and a current of CO_2-free air kept passing through the apparatus for 30 minutes. The increase of weight of the soda lime or caustic potash corresponds to the weight of carbon dioxide, which is to be calculated to percentage of sample as received.

Silica and Insoluble.—Place 0.5 g. of the sample prepared as described above in a porcelain casserole. Add about 25 ml. of 1 : 5 HCl, and evaporate to apparent dryness on a hot plate. Cool and add enough concentrated HCl to wet thoroughly. Add about 10 ml. of water, boil, filter, and wash. Put the filtrate back in the same casserole. Evaporate it to dryness and heat to about 120° C. for one hour. Cool. Add enough concentrated HCl to wet thoroughly. Add about 25 ml. of water, boil, filter, and wash. Transfer the two papers containing the two precipitates to the same crucible, ignite, and weigh. Calculate this weight to percentage of sample as received.

Iron and Alumina.—To the filtrate obtained above, add a few drops of HNO_3 and boil to insure oxidation of the iron. Add 2 g. of NH_4Cl previously dissolved in water. Make alkaline with NH_4OH. Digest hot for a few minutes until the precipitate coagulates. Filter, wash, ignite the precipitate and weigh as $Fe_2O_3+Al_2O_3$. Calculate this weight to percentage of sample as received. This precipitate may be further treated to separate the two oxides, but this is generally unnecessary. (N. B. precautions if PO_4 or F are present under Estimation.)

Lime.—(*a*) To the filtrate obtained above, add 5 g. of $(NH_4)_2C_2O_4$ dissolved in water. Digest hot for ½ hour, making sure that the solution is always

alkaline with NH_4OH. Filter, wash and ignite in a platinum crucible over a strong blast to constant weight. Calculate this weight to percentage of sample as received. See under Estimation for precautions.

(*b*) **Alternative Method.**—To the filtrate obtained from the iron and alumina precipitates, add 5 g. of $(NH_4)_2C_2O_4$ dissolved in water. Digest hot for $\frac{1}{2}$ hour, making sure that the solution is always alkaline with NH_4OH. Filter and wash. Transfer the precipitate to a beaker, and wash the filter paper with hot dilute H_2SO_4, catching the washings in the same beaker. Heat gently to complete solution, adding more H_2SO_4 if necessary. While still warm titrate with a solution of $KMnO_4$ containing 5.6339 g. per liter, until the pink color is permanent. The number of milliliters of $KMnO_4$ used gives directly the percentage of lime in the dried sample. Recalculate to percentage of sample as received.

Magnesia.—To the filtrate obtained from calcium precipitate, add enough water to give a total volume of about 600 ml. Cool. Add 10 ml. of NH_4OH and 5 g. $NaNH_4HPO_4$ dissolved in water. Stir until precipitate begins to form. Let stand over night. Filter, wash with a 2.5 per cent by weight solution of NH_4NO_3. Ignite and weigh. Multiply this weight by 0.36207 to find the weight of MgO. Then calculate to percentage of sample as received.

Sulfur Trioxide.—Dissolve 0.5 g. of the sample prepared as described in Section on Combined Water in 50 ml. of 1 : 5 HCl. Boil. Add 100 ml. of boiling water, and continue boiling for 5 minutes. Filter immediately and wash thoroughly with hot water. Boil, and while boiling, add slowly 20 ml. of a boiling 10 per cent solution of $BaCl_2$. Digest hot for one hour, or until precipitate settles. Filter and wash. Dry carefully. Ignite over Bunsen burner at lowest heat possible until filter paper is burned off. Ignite at bright red heat for 15 minutes, and weigh. Multiply this weight by 0.34297 to determine the weight of SO_3. Then calculate to percentage of sample as received.

Sodium Chloride.—Dissolve in boiling water a 1-g. sample (prepared as described in Section on Combined Water), put on the filter and wash with 250 ml. of boiling water, then titrate the filtrate. Add two or three drops of potassium chromate solution and titrate with an N/20 solution of silver nitrate. Each milliliter of silver nitrate solution = 0.002923 g. of sodium chloride. Calculate to percentage of sample tested.

Calculation of Results.—By the methods given above, the results are obtained and reported in the following form:

	Per Cent
Free water..	
Combined water..	
Silica and insoluble, SiO_2..	
Iron and alumina, R_2O_3..	
Lime, CaO..	
Magnesia, MgO..	
Sulfur Trioxide, SO_3..	
Carbon Dioxide, CO_2..	
Sodium Chloride, NaCl..	
	100.00±

NOTE.—Since it is frequently advisable to recalculate these results, that they may be more enlightening, the following method is submitted for consideration:

(a) Multiply percentage of MgO by 2.0912 to find percentage of $MgCO_3$.

(b) Multiply the percentage of MgO by 1.09[illegible] to find the percentage of CO_2 as $MgCO_3$.

(c) Deduct CO_2 as $MgCO_3$ from the CO_2 determined.

(d) Multiply the CO_2 remaining by 2.2742 to find percentage of $CaCO_3$.

(e) Add together the percentage of SiO_2, R_2O_3, $MgCO_3$, and $CaCO_3$, and report in the aggregate.

(f) Multiply the percentage of $CaCO_3$ by 0.56031 to find the percentage of CaO as $CaCO_3$.

(g) From the total percentage of CaO deduct the percentage of CaO as $CaCO_3$. The remainder may be called "available CaO."

(h) The "available CaO" should bear to the SO_3 a ratio of 0.6991 to 1. Determine which (if either) is in excess.

(i) If the CaO is in excess, multiply the SO_3 by 0.6991, and subtract the result from the "available CaO." The remainder is reported as "excess CaO."

(j) If the SO_3 is in excess, multiply the "available CaO" by 1.4304 and subtract the result from the SO_3. The remainder is reported as "excess SO_3."

(k) Add together the "available CaO" and the SO_3, and subtract the "excess CaO" or "excess SO_3." The remainder is $CaSO_4$.

(l) If the $CaSO_4$ is present as $CaSO_4 \cdot \frac{1}{2}H_2O$, the percentage of $CaSO_4$ should bear to the percentage of combined water a ratio of 15.12 to 1. Determine which (if either) is in excess.

(m) If the $CaSO_4$ is in excess, some of it is present in the anhydrous form. Multiply the percentage of combined water by 15.12 to find the percentage of $CaSO_4$ as $CaSO_4 \cdot \frac{1}{2}H_2O$. The difference between the total $CaSO_4$ and the percentage of $CaSO_4$ as $CaSO_4 \cdot \frac{1}{2}H_2O$ is the $CaSO_4$ in the anhydrous form.

(n) If the water is in excess, some of the $CaSO_4$ is present as gypsum. Let x = percentage of $CaSO_4 \cdot \frac{1}{2}H_2O$, and y = percentage of $CaSO_4 \cdot 2H_2O$. Then $x+y$ = percentage of $CaSO_4$ (as found in k) + percentage of water.

$$0.06206x+0.2093y = \text{percentage of combined water.}$$

Solve these equations for x and y. Report x as percentage of "calcined gypsum," $CaSO_4 \cdot \frac{1}{2}H_2O$. Report y as percentage of gypsum, $CaSO_4 \cdot 2H_2O$.

Having made these calculations, the result may be reported as follows:

	Per Cent
Gypsum, $CaSO_4+2H_2O$	
Calcined gypsum, $CaSO_4+\frac{1}{2}H_2O$	
Anhydrite, $CaSO_4$	
Excess CaO or Excess SO_3	
Sodium chloride, NaCl	
Other ingredients	
	100.00±

The presence of the different forms of $CaSO_4$ may be corroborated by a microscopic examination.

OTHER GRAVIMETRIC METHODS

Calcium may be converted to carbonate, sulfate, fluoride, tungstate and so weighed. The oxide, obtained by ignition of the oxalate may be converted to sulfate by moistening with a few drops of H_2SO_4, then adding an excess of NH_4OH and igniting to expel excess of sulfate and NH_3.

Calcium sulfate may be precipitated by adding an excess of H_2SO_4 and then 95% alcohol (two to four times the total volume of the solution). The precipitate is washed with alcohol and then ignited to constant weight. (Fresenius.)

Calcium tungstate by Saint Sernin's method is precipitated by adding

ammonia until the solution is alkaline and then an excess of 20% solution of sodium tungstate. The precipitate is best filtered into a weighed Gooch crucible and washed with ammonia (1 : 10 soln.) then dried at 100° C. and weighed as $CaWO_4$.

DETERMINATION OF CALCIUM IN WATER. VOLUMETRIC PERMANGANATE METHOD

The hardness of water is due largely to the presence of calcium and magnesium carbonates or bicarbonates. Calcium may be determined volumetrically by precipitation as oxalate and titration in an acid solution by standard potassium permanganate, according to the reaction:

$$5CaC_2O_4+2KMnO_4+8H_2SO_4=5CaSO_4+K_2SO_4+2MnSO_4+8H_2O+10CO_2.$$

In the gravimetric method it is necessary to remove SiO_2, Fe_2O_3 and Al_2O_3 before precipitating CaC_2O_4. Ferrous iron alone titrates so that it is necessary only to make provision for iron in case it is present in appreciable amount.

Procedure.—Measure a 250 ml. portion of the water to be examined by means of a 250-ml. graduated flask into a 400-ml. beaker. Add 1 ml. of HCl (sp. gr. 1.2) and evaporate to half its volume if the water is considerably hard or to about one-fifth its volume if it is moderately hard. By means of a dropper add 4–5 drops of methyl red and then ammonium hydroxide drop by drop until a reddish-yellow color appears. If a precipitate appears just dissolve in a drop or so of HCl. If iron is indicated add 2–3 small crystals of citric acid. (This should be ample. A large excess is not desired.) The solution will now be faintly acid. Heat to boiling and add slowly about 25–30 ml. of a saturated solution of oxalic acid. Boil for a few minutes, make alkaline with NH_4OH and allow to settle.

Filter and wash the filter free of the oxalate reagent. (Twenty ml. of the wash water should not decolorize 1 drop of N/10 $KMnO_4$ reagent.) Open out the filter on a beaker cover, and hold slanting over a beaker. By means of a stream of 10% H_2SO_4 dissolve off the precipitate into the beaker, using about 50 ml. of the dilute acid. Now rinse off into the beaker by means of about 50 ml. of water, the acid clinging to the filter.

Heat the solution in the beaker to boiling and titrate with N/10 $KMnO_4$ until a faint pink color appears.

One ml. N/10 $KMnO_4$ is equivalent to 0.002 g. Ca. Report results in parts per million, first as Ca and also as $CaCO_3$.

NOTE.—In water containing considerable magnesium it may be necessary to dissolve the precipitate in HCl and reprecipitate as CaC_2O_4 to purify the precipitate from occluded magnesium as in the gravimetric method.

Conversion factors. $Ca\times2.5=CaCO_3$; 1 liter $=0.264$ gallon. 1 gram $=15.43$ grains. Convert above results to grains per gallon.

CARBON

C, *at.wt.* 12.01; *sp.gr. amorp.* 1.75–2.10; *cryst.: graphite*, 2.25; *diamond*, 3.47–3.5585; *m.p. sublime at* 3500° C.; *oxides*, CO *and* CO_2

Carbon occurs free in nature in the forms—diamond, graphite, and amorphous carbon. It occurs combined widely distributed in organic compounds in the animal and vegetable kingdoms in combination with hydrogen, oxygen, nitrogen and other elements. As hydrocarbons it occurs in natural gas, petroleum and bitumen. As carbon dioxide in the air and confined under pressure in pockets in the earth. It occurs as carbonate in rocks combined principally with calcium, magnesium and iron.

DETECTION

Element.—Carbon is recognized by its appearance and by its inertness towards general reagents. It is seen in the charring of organic matter when heated or when acted upon by hot concentrated sulfuric acid.

Upon combustion with oxygen or by oxidation with chromic and sulfuric acids, carbon dioxide is formed. The gas passed into lime water forms a white precipitate, $CaCO_3$. Penfield fuses the substance with precipitated and washed $PbCrO_4$ in a hard glass tube closed at one end. The CO_2 is tested at the mouth of the tube.

Carbon Dioxide. Carbonates. CO_2 in Gas.—A white precipitate with lime water, baryta water, ammoniacal solutions of calcium, or barium chlorides, or lead acetate (basic), carbonates of the metals are formed.

Carbonates.—Action of mineral acids causes effervescence, CO_2 being evolved. The gas is odorless (distinction from SO_2, H_2S, and N_2O_3) and is colorless (distinction from N_2O_3). See test for CO_2 above.

Distinction between Soluble Carbonates and Bicarbonates.—The solution of the former is alkaline to phenolphthalein indicator (pink). Bicarbonate solutions remain colorless with this indicator. Normal carbonates precipitate magnesium carbonate when added to magnesium sulfate solution; bicarbonates cause no precipitation.

Free Carbonic Acid in Water in Presence of Bicarbonates.—0.5 ml. of rosolic acid (1 part acid in 500 parts of 80% alcohol), produces a red color with

bicarbonates in absence of free CO_2, and a colorless or faintly yellow solution when free CO_2 is present.

Carbon Monoxide.—The gas burns with a pale blue flame and is not absorbed by potassium hydroxide or lime water (distinction from CO_2). It is oxidized to CO_2 and so detected. With hot, concentrated potassium hydroxide, potassium formate is produced.

The gas is detected in the blood by means of the absorption spectrum.

The gas colors a mixture of I_2O_5 and fuming sulfuric acid (on a support of pumice) a transient green (Hoover and Lamb. " Hoolamite detector ").

ESTIMATION

Among the substances in which the determination of carbon is commonly made are the following:—organic compounds, carbonate rocks and minerals—such as calcite, marble, limestone, dolomite, magnesite, witherite, spathic iron ore; commercial products such as cement, soda and baking soda; alloys including carbon in steel; carbon dioxide in gases including air. A special chapter is devoted to gas analysis.

PREPARATION OF THE SAMPLE

Iron, Steel, and Alloys.—The subject is discussed in the chapter on Iron and Steel, Volume II.

Organic Matter.—It is advisable to fuse this in a nickel or iron crucible with sodium peroxide. The carbonate thus formed may be determined as usual. The organic substance may be oxidized directly in the combustion furnace.

Carbonates. Limestone, Dolomite, Cement, Alkali Carbonates and Bicarbonates.—The powdered material is decomposed by addition of an acid as directed in the methods given later.

SEPARATIONS OF CARBON FROM OTHER SUBSTANCES

The element is generally determined as carbon dioxide, in which form it is liberated from most of the combinations in which it occurs, free from other substances by ignition in a current of oxygen, or by oxidation with chromic acid as directed later.

Separation of Carbon in Iron and Steel. Cupric Potassium Chloride Method.—0.5 to 2 grams of the drillings are treated with 100 to 200 ml. of cupric potassium chloride solution and 10 ml. of hydrochloric acid (Sp. Gr. 1.19). This mixture dissolves the iron according to the reaction,

$$Fe + CuCl_2 = FeCl_2 + Cu \text{ and } Cu + CuCl_2 = Cu_2Cl_2 + \text{carbon as a residue.}$$

The solution should be stirred frequently to hasten the solution of the iron. It is advisable to keep the temperature of the solution at about 50° C. When the iron and copper have dissolved the carbon is filtered off into a perforated platinum boat or crucible, as directed under the methods. It is now oxidized to CO_2 and so determined.

NOTE.—The cupric potassium chloride solution is prepared by dissolving 150 parts of potassium chloride and 170 parts of crystallized cupric chloride in water and crystallizing out the double salt. Three hundred grams of this salt are dissolved in 1000 ml. The solution may be used several times by chlorinating the dirty brown filtrate from the carbonaceous residue. The cuprous chloride formed during the solution of the steel is converted again to cupric chloride, and the chlorinated double salt is even more energetic in its solvent action than the freshly made reagent. (Blair.)

In Presence of Sulfur.—SO_2 is oxidized to SO_3 by passing the hot gases from the carbon combustion through ignited lead chromate with the resulting formation of the non-volatile lead sulfate. The SO_2 may also be removed by passing the gases (CO_2 and SO_2) through a concentrated solution of chromic and sulfuric acids; SO_2 oxidized to SO_3 remains in the solution, while CO_2 is not absorbed and passes through.

GRAVIMETRIC METHODS FOR DETERMINATION OF CARBON

The determination of carbon gravimetrically depends on conversion to carbon dioxide and weighing the gas. This is accomplished by absorption of the CO_2 in a suitable reagent. Carbon is converted to the dioxide by oxidation either by means of a fluid oxidizing reagent or by combustion in presence of air or oxygen. Details for carbon in steel and alloys and in organic matter follow. Carbon combined in carbonates is generally determined by decomposition with an acid and determining the CO_2 by absorption—direct method—or by the loss of weight in the substance due to evolved CO_2-indirect method or loss of weight method—details follow later.

DETERMINATION OF CARBON BY COMBUSTION

Apparatus. Combustion Furnace.—Although the gas furnace has been used more commonly on account of gas being more available than electricity, the extension of generating electric plants makes it possible to use electric furnaces, and these are displacing those heated by gas, as they are more compact, easily manipulated and comparatively simple in structure.

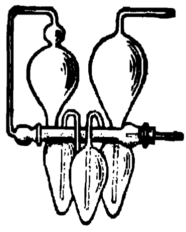


FIG. 20.—Geissler Bulb.

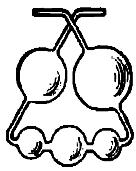


FIG. 21.—Liebig Bulb.

A simple electric furnace may be made by wrapping a silica tube with a thin covering of asbestos paper, which has been moistened with water. On drying the paper will cling to the tube. A spiral coil of nichrome wire (Driver and Harris) is wound around this core. On a 2-foot length of tube two 45-foot lengths of No. 18 wire, connected in parallel, will heat the tube to bright redness,

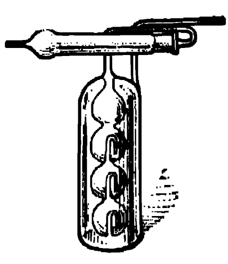


FIG. 22.—Gerhardt Bulb.

FIG. 23.—Vanier Bottle.

if 110 volts A.C. are applied. The coils should be covered with $\frac{1}{4}$-in. coating of alundum cement. For appearance' sake as well as for protection, the tube is placed in a large cylinder of sheet iron, packed around with asbestos, and is held in position by circular asbestos boards placed at the ends of the large cylinder. The cylinder is mounted on a stand.

Absorption Apparatus.—A large number of forms may be obtained. The Geissler and Liebig bulbs have been popular (Figs. 20 and 21), but are now being displaced by forms that have less surface exposed, that are more easily cleaned and less fragile, such as Gerhardt's, Vanier's, using solutions of NaOH or KOH, or Fleming's and Stetser's type of apparatus, using solids. (Figs. 22–24).

Details of the Absorption Apparatus.—Figure 24, is Fleming's modification of Mr. Martin's apparatus. When properly filled this tube will serve for at least 70 combustions when operating on 1.5 grams of sample containing 1.03% carbon.

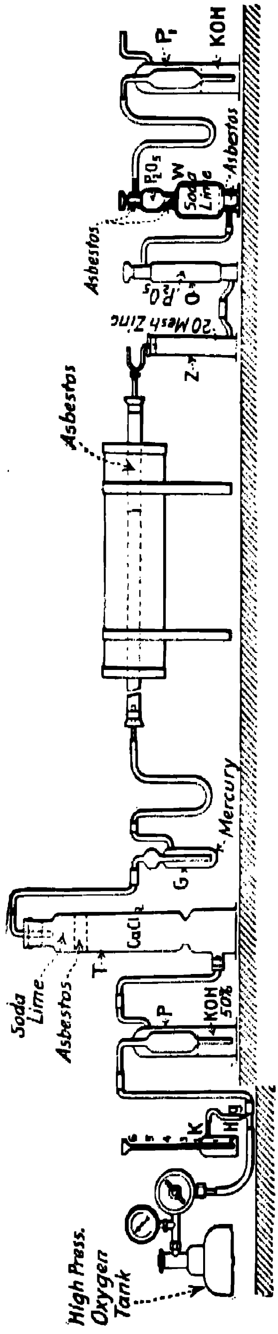


FIG. 24.—Fleming Absorption Apparatus.

The anhydride in the upper chamber serves for at least 300 combustions. Soda lime, placed in the lower tube in alternate layers ($\frac{1}{8}$ in.) of the different meshes, has proven a very convenient and desirable reagent. The 12-mesh soda lime for nitrogen can also be used with excellent results. If this is employed, part of it should be ground to about 60-mesh and alternate layers of fine and coarse used.

Purification and Absorption Trains.—Details of these are given in the portion of this chapter under the Determination of Carbon in Steel.

DETERMINATION OF CARBON IN ORGANIC SUBSTANCES

COMBUSTION OF ORGANIC SUBSTANCES FREE OF NITROGEN, HALOGENS, SULFUR, AND THE METALS

Carbon is determined by combustion to CO_2, the gas absorbed in a suitable reagent, such as caustic soda, soda lime, soda asbestos (ascarite), contained in a convenient form of apparatus. The combustion is made in a tube (a form is shown below) heated to redness, by passing pure oxygen or air (free from moisture and CO_2) over the material. A description of the purification and absorption train is given under the section devoted to carbon determination in steel, in the following portion of this chapter. Usually hydrogen is determined at the same time as carbon, as it is necessary under any circumstance to take care of the moisture formed and prevent it from entering the absorption chamber. The same moisture absorbent for drying the gas entering the combustion chamber is used as for absorbing the moisture formed by combustion. This

drying agent should not absorb CO_2. The following agents are satisfactory:—concentrated sulfuric acid, magnesium perchlorate trihydrate, phosphorus pentoxide. It is advisable to have the moisture absorbent preceded by an empty tube in which most of the water can be condensed to prolong the effectiveness of the reagent.

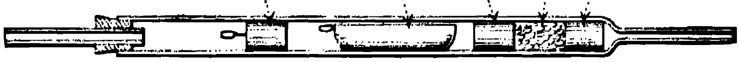


FIG. 25

Details of the Combustion Tube for Determining Carbon and Hydrogen in Organic Matter.

The combustion tube (Fig. 25) is about 95 cm. in length with an internal diameter of about 12–15 mm. Three copper gauze rolls, copper oxide with lengths of columns appear in the figure above. Substances that contain halogens, nitrogen or sulfur require special reagents (not shown) in the combustion tube. For example lead chromate is substituted for copper oxide, when halogens and sulfur are present; a reduced copper roll is used at the exit end of the tube when nitrogenous compounds are present. The exit end of the tube is cooled by wrapping a strip of absorbent material about the tube and dipping the free ends in a beaker of water.

PROCEDURE

The apparatus is first swept out with pure oxygen to remove any moisture or CO_2. The water absorption bulbs and the CO_2 absorption bulbs are weighed. To take care of the error caused by air buoyancy similar apparatus is placed on the opposite pan as a counter balance, this apparatus being slightly lighter than the absorption apparatus. For example if a Fleming's apparatus is used for absorption of CO_2, a slightly lighter Fleming's apparatus is used as a counter balance.

It is often advisable to mix intimately the material that is being examined with about ten times its weight of powdered lead chromate and an equal amount of potassium chromate when the material contains much inert substance,[1] for example in determining organic matter in rocks and minerals. This is generally not required by pure organic substances.

Solids are placed directly in the combustion boat, weighing being conducted, if desired, in the previously weighed boat. Liquids are weighed in glass bulbs. The glass bulb may be blown, a capillary end drawn out and the weighing conducted during the sweeping out of the furnace. It is filled by heating the bulb, placing the capillary tip in the liquid and then cooling. The tip is wiped off and sealed in the flame and the bulb and contents again weighed. Just before placing in the boat and inserting in the combustion tube the tip of the capillary is filed off. Substances burning with difficulty can be burned by mixing with powdered CuO, which has been previously ignited.

The combustion tube, swept free of CO_2 and moisture, is prepared for the combustion run by heating the section of the tube containing the copper oxide to redness, at the same time keeping the portion zoned for the combustion boat cool, the 12 cm. gauze plug (Fig. 27) being removed. The sample, placed in the

[1] *Caution.*—$PbCrO_4$ melts and decomposes at 600° C., K_2CrO_4 fuses at 971° C.

boat, is now inserted in the combustion tube, the capillary tip pointing towards the open end of the tube, the 12 cm. copper gauze plug replaced and the tube quickly closed. The current of oxygen is immediately turned on and the run started, all the apparatus being connected and free of leaks. (See Determination of Carbon in Steel.) After a few minutes the portion of the tube containing the sample is gradually heated to redness (600–800° C.) and the run continued until the combustion is complete. Some experience and skill is necessary for correct results. The combustion of solids should be conducted slowly, liquids require a slightly more rapid flow of gas to furnish sufficient oxygen before any vapor escapes from the oxidizing zone. The tube is allowed to cool with the oxygen flowing through the apparatus. If hydrogen is also being determined, it may be necessary to sweep forward any condensed moisture in the apparatus previous to the moisture absorption tubes by heating with a naked flame, starting near the exit end of the combustion tube and carrying the heat cautiously towards the absorption tubes.

The absorption bulbs are weighed with the tare weights as recommended. Increase of weight is due to H_2O and CO_2 in the respective apparatus.

$$H_2O \times 0.1119 = H.$$
$$CO_2 \times 0.2729 = C.$$

Carbon in Soils.—One to 3 grams of 60-mesh sample is treated with a solution of 3.3 grams CrO_3+10 ml. H_2O and 50 ml. conc. H_2SO_4 (Sp. Gr. 1.84). The evolved CO_2 is absorbed in standard caustic and titrated with acid, phenolphthalein and methyl orange being used as indicators. (J. Ind. Eng. Chem., **6**, 843–846, 1914.)

Carbon in Minerals.—Fusion in the combustion tube with granulated lead chromate is recommended for oxidation of the carbon. (10 parts $PbCrO_4$+1 part K_2CrO_4.)

NOTE.—The oxygen gas should be free from hydrogen. A preheater, placed before the purifying tubes of the train, causes the combustion of the hydrogen and the absorption of the water formed before the gas enters the combustion tube.

DETERMINATION OF CARBON AND HYDROGEN IN NITROGENOUS SUBSTANCES

A modification of the first procedure described for determinations of carbon and hydrogen in organic substances must be made, since from substances containing nitrogen, nitroso and nitro compounds, oxides of nitrogen are formed which would be absorbed in the calcium chloride and potash bulbs, giving high results for hydrogen and carbon. To overcome this difficulty, a copper spiral, that has been reduced (See note below) is placed in the front end of the combustion tube (to the right in Fig. 25) to reduce the oxides of nitrogen to nitrogen.

NOTE.—Reduction of copper spiral may be accomplished as follows: The copper spiral is prepared by rolling together a piece of copper gauze about 10 centimeters wide, making it as large as will conveniently pass into the combustion tube. The spiral is heated till it glows by holding it in a large gas flame, and while still hot it is dropped into a test-tube containing 1 or 2 ml. of methyl alcohol or ether. This quickly boils away, igniting at the end of the tube. The copper is completely reduced to bright metallic copper. The spiral is taken out with a pair of crucible tongs and dried by quickly

passing it through a flame a few times, and while it is still warm it is introduced into the front of the combustion tube.

The substance is introduced into the tube and the connections made. The copper oxide spiral, that was pushed after the boat, is heated, and then the reduced spiral (right end of tube). The oxide near the boat, and finally the entire tube is heated to a red heat. When the bubbles cease to show in the potash bulb, the stopcock is opened to the oxygen-purifying train and a slow flow of oxygen turned on, the gas allowed to pass through the tube until it can be detected with a glowing splinter at the exit of the absorption end of the apparatus.

If the substance is difficult to burn, it is mixed with freshly ignited (cold) copper oxide, which assists combustion.

The remainder of the operation is the same as has been described.

ORGANIC SUBSTANCES CONTAINING HALOGENS

The procedure is the same as that described for nitrogenous substances with the exception that a silver spiral is used in place of the reduced copper spiral. The heating of this spiral should be between 180 and 200° C. (not over 200°).

ORGANIC SUBSTANCES CONTAINING SULFUR

These are best ignited with sodium peroxide and the carbonate formed is determined by the procedure given for carbon dioxide in carbonates.

To oxidize the SO_2 that forms, lead chromate is used in place of copper oxide in the combustion tube, a lower temperature being necessary to prevent fusion of the chromate. The SO_2 is oxidized to SO_3, which reacts with the lead forming the non-volatile $PbSO_4$, while CO_2 is not acted upon and passes on. See also separations under Estimation.

Micro Methods for the determination of the elements in organic compounds are described in detail in a chapter on this subject in Vol. II.

Semi-Micro Method for Carbon and Hydrogen.—A systematic development of methods for the ultimate analysis of 20–50 mg. samples has been given by H. Ter Meulen, J. Heslinga and other investigators.[2] This field of work has

[2] H. Ter Meulen, Estimation of Oxygen in Organic Compounds, Rec. Trav. Chim. **41**, 509 (1922).

H. Ter Meulen and J. Hesslinga, Halogens, ibid. **42**, 1093 (1923); **43**, 181 (1924).

J. Hesslinga, Estimation of C, H and N, ibid. **43**, 551 (1924).

H. Ter Meulen, Estimation of N by Hydrogenation, ibid. **43**, 643 (1924). Estimation of O by Hydrogenation, ibid. **43**, 899 (1924). See also, ibid. **44**, 271 (1925); **45**, 365 (1923); **45**, 368 (1926), for Determination of N, As and Hg respectively.

P. Maes, Determination of Nitrogen, Chem. Abs. **29**, 2474 (1935).

Wilson and Sun, C. H., J. Chinese Chem. Soc. **2**, 129 (1934); Chem. Abs. **29**, 76 (1935).

E. P. Clark, Semi-Micro Technique, J. Assoc. Off. Agr. Chem. **16**, 255 (1933).

H. Ter Meulen, Analysis by Hydrogenation and some Oxidation Methods, Rec. Trav. Chim. **53**, 118 (1934).

R. Roger and W. MacKay, J. Soc. Chem. Ind. **54**, 46T (1935).

W. W. Russell and J. W. Fulton, Determination of Oxygen, Ind. Eng. Chem., Anal.

been noteworthy because of the application of active catalysts for oxidation or hydrogenation.

Method.—The whole apparatus is very small and compact; suitable dimensions are indicated below, Fig. 26. The catalytic MnO_2 is prepared by mixing $MnSO_4$ and $KMnO_4$ in nitric acid solution in the ratio 2 mols : 3 mols. The MnO_2 is washed by decantation, with distilled water, collected, compressed and cut into pellets about 0.2–0.5 cm. in diameter, dried in an air bath at 100° and finally heated for 30 minutes at 300° C. The fine material is screened out. If oxygen rather than air is used for the combustion of the organic compound, an active catalyst may be used for many successive determinations; if air is used then a catalyst filling lasts for about five determinations. In any event the filling should be renewed when ⅔ of it has turned yellowish brown indicating loss of available oxygen.

DETAILS OF FILLINGS FOR THE COMBUSTION TUBE

The Compound contains:	Catalyst for Oxidation:	Temp. of Catalyst	Notes
(1) C, H, O.	MnO_2 6 cm. long	400°	Must not be heated above 450°.
(2) C, H, O, Halogen	MnO_2 & PbO_2 1 : 1 6 cm. length	400°	Active life longer than for (1).
(3) C, H, O, S	MnO_2 8 cm. long (PbO_2 is added if halogen is present)	6 cm. at 400° 2 cm. at 150–180°	Part of the catalyst projects beyond the furnace to cool it.
(4) C, H, O, N	MnO_2 6 cm.; PbO_2 2 cm. (PbO_2 is mixed with the MnO_2 if the compound contains halogen.)	MnO_2 at 400°	The PbO_2 layer is outside of the heated zone and its temperature is below that at which is loses oxygen.

After the apparatus has been assembled and tested for blank correction, which should be practically negligible, with a 4 bubble per second stream of oxygen, the weighed substance is introduced in a platinum boat, and very slowly distilled to the catalyst by gentle heating with a micro burner. The combustion requires 15–25 minutes for 0.05 g. of material. The heating unit is moved to the left and any unburned carbon near the catalyst is heated by a suitable burner, and finally care is taken to drive any condensed moisture into the first U-tube.

THE WET COMBUSTION PROCESS FOR DETERMINATION OF CARBON

The method depends upon the oxidation of carbon to carbon dioxide when the powdered material is digested with a mixture of concentrated sulfuric acid and chromic acid, or potassium dichromate, or permanganate. The pro-

Ed. 5, 384 (1933); Also Russell and M. E. Marks, ibid. 6, 381 (1934); 8, 453 (1936); M. E. Marks, ibid. 7, 102 (1935).

E. P. Griffing and C. L. Alsberg, Nitrogen, J. Am. Chem. Soc. 53, 1037 (1931).

H. Ter Meulen and J. Heslinga, Neue Methoden der Organisch-Chemischen Analyse, Akademische Verlagsgesellschaft, Leipzig, 1927. Nouvelles Methodes d'Analyse Organique, Dunod, Paris, 1932.

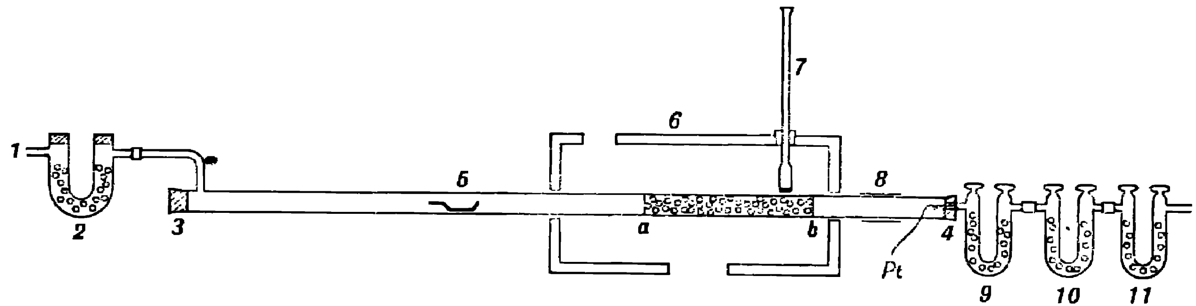


FIG. 26.—Ter Meulen-Hesslinga Apparatus for Carbon-Hydrogen Determination.

1. Inlet for purified air or oxygen.
2. U-tube for drying the gas.
3–4. Quartz combustion tube 32 cm. long and 0.8 cm. inner diameter.
5. Platinum boat.
6. Oven (electric or gas) 12 cm. long by 6 cm. diam. The oven may be moved along nearly to the end of the tube, 3.
7. Nitrogen-filled thermometer or thermocouple.
8. Metal sleeve to aid in keeping material heated to 150–180° C.

Pt indicates platinum wire placed in side arm of U-tube 9, to aid in driving condensed water into 9.

a–b Catalyst. The oven 6 and sleeve 8 may be moved so that 2 cm. or so of the catalyst is at the right of the oven (see text).

9. U-tube filled with the same drying agent as was used in tube 2. Calcium chloride or more effective desiccants may be used.
10. U-tube with left $\frac{2}{3}$ filled with ascarite and right $\frac{1}{3}$ filled with the same desiccant used in tube 9.
11. Guard tube filled with the same desiccant as is used in tube 9.

cedure is applicable to oxidation of free carbon, carbon combined in organic substances and in certain instances to carbon combined with metals, where the substance may be decomposed by the action of the acids.[3] It is of value in determination of carbonates in presence of sulfides, sulfites, thiosulfates and nitrites, which would vitiate results were they not oxidized to more stable forms, before passing into the potash bulb with the carbon dioxide.

Apparatus.—The apparatus is identical with that used for determining carbon dioxide in carbonates, Fig. 34, with the exception that in place of the acid bulb nearest the decomposition flask two bulbs are placed. The first of these contains a strong solution of chromic and sulfuric acids, the second is filled with glass beads moistened with chromic acid solution. Following this is the drying bulb containing concentrated sulfuric acid and finally the absorption apparatus, as shown in the illustration.

Procedure.—0.2 to 1 gram of the powdered material, fine drillings, free carbon, or organic substance is placed in the decomposition flask. If the material is apt to pack it is advisable to mix with it pure ignited sea-sand to prevent this. Five to 10 grams of granular potassium dichromate are added and the apparatus swept free of carbon dioxide by passing purified air through it before attaching the absorption apparatus. The potash bulb is now weighed, using a counterbalance bulb and following the precautions given in the dry-combustion method. The bulb is attached to the train.

Oxidation.—Concentrated sulfuric acid placed in the acid funnel, attached to the decomposition flask, is allowed to flow down on the sample until the funnel is almost empty; the stop-cock is then closed. A flame is placed under the flask, when the vigorous action has ceased, and the material gently heated until the reaction is complete and the organic matter or carbon completely oxidized.

The apparatus is now swept free of residual CO_2 by applying suction, the gas being completely absorbed by the potash, or the soda lime reagent.

The increase of weight of the absorption bulb is due to carbon dioxide.

$$CO_2 \times 0.2729 = C.$$

NOTE.—The following additional purifiers are frequently advisable: (*a*) an absorption bulb containing silver sulfate to absorb chlorine and vapors from sulfur compounds; (*b*) a capillary tube of silica or platinum heated to a dull redness to oxidize any hydrocarbons, carbon monoxide, etc., that may be evolved and imperfectly oxidized by the chromic acid.

[3] Not applicable for determining carbon in ferro-silicon, ferro-chrome or tungsten.

DETERMINATION OF CARBON IN STEEL

STETSER AND NORTON COMBUSTION TRAIN FOR CARBON DETERMINATIONS

Carbon is added to steel to increase its hardness. With over 1 per cent of carbon the steel becomes brittle.

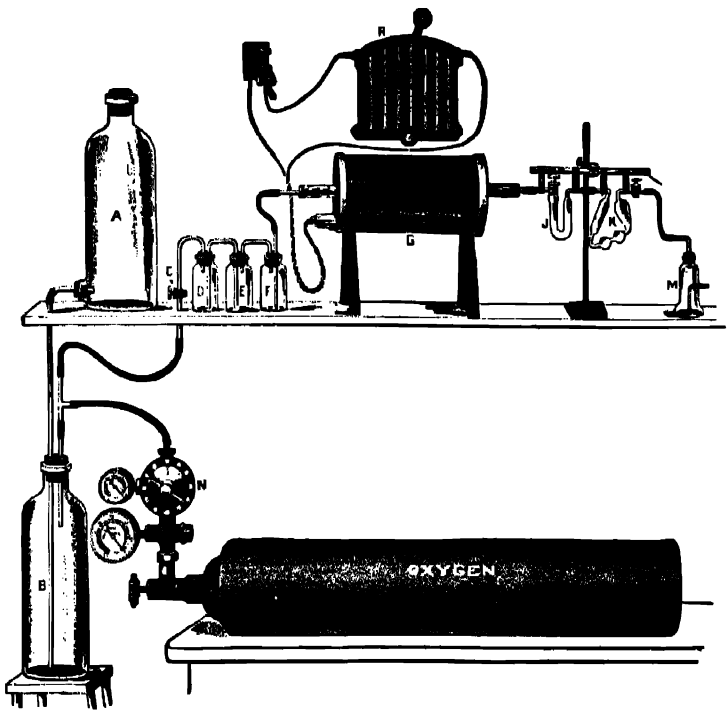


FIG. 27.—Stetser and Norton Combustion Train for Carbon Determinations.[1]

A **Aspirator Bottle,** 8 liters capacity, graduation interval 250 ml., with one hole rubber stopper.
B **Bottle,** narrow mouth, of green glass, 2 gallons capacity, with two hole rubber stopper.
Glass Tubing, 6 mm. outside diameter, for connections.
Glass T-tube, 3 mm. bore.
C **Glass Stopcock,** 2 mm. bore; used to prevent the gas from flowing through the train when turned on at the regulator.
D **Bottle,** wide mouth, 8 oz. capacity, with two hole rubber stopper; to be used empty as a safety.
E Ditto; to be filled one-third full with concentrated sulfuric acid.
F Ditto; to be filled with ascarite with a layer of anhydrone or P_2O_5, to absorb the water set free on absorption of CO_2 by ascarite.
Combustion Tube, of Silica, glazed, 30 inches long by $\frac{7}{8}$ inch diameter.
G **Combustion Tube Furnace.**
R **Rheostat,** for controlling the temperature.
J **Vanier Zinc Drying Tube;** to be filled with 30 mesh zinc.
K **Vanier Sulfuric Acid Bulb;** to be half filled with sulfuric acid.
M **Stetser and Norton Modification of the Midvale Absorption Bulb.**

[1] By courtesy of Arthur H. Thomas Co.

COMBUSTION METHOD

The train illustrated in Fig. 27 was described by J. B. Stetser and R. H. Norton in "*Combustion Train for Carbon Determinations,*" The Iron Age, Vol. 102, No. 8. The special features of this outfit are rapidity with which combustions can be made, simplicity of the absorption bulb, and the use of ascarite, a special sodium hydrate asbestos absorbent mixture according to the formula of Mr. J. B. Stetser. It is a dryer as well as an absorber.

The absorption bulb is a modification of the Midvale Absorption Bulb designed by Mr. H. L. Fevert, of the Midvale Steel Company, and with one filling can be used for at least 400 determinations using one-half factor weight with carbon 0.50%. The bulb measures 45 mm. in diameter at its widest portion at the bottom, and 120 mm. high over all. It is provided with a capillary tube and rubber stopper at top, or with ground glass stopper.

The usual procedure is to allow three or four minutes for combustion. Results are often reported in six minutes after the sample enters the laboratory: this includes time for drilling, weighing sample, running test, weighing bulb and reporting result.

The oxygen is delivered from a high pressure cylinder through the gas pressure regulator, and the authors also recommend that bottles as shown in the illustration be used to measure the amount of gas consumed and to supply rapidly the extra quantity of oxygen required during the burning of the drillings, in addition to equalizing the pressure.

Method of Operation.—The train is set up free from leaks, and the stopcocks are opened with the exception of the one on the Sulfuric Acid Bulb K. This is opened sufficient to allow gas to flow at the rate of 200 to 250 ml. per minute when the Absorption Bulb is attached.

The stopcock C is then closed, the remaining stopcocks being left as adjusted. The train is now ready for operation. Bottle B is filled with water. The gas regulator is opened, allowing oxygen to displace the water in bottle B, which water is driven into bottle A. When bottle A is filled, the regulator is closed and the train is ready for combustion. The exit end of the combustion tube, the usual glazed silica tube being recommended, is packed with some asbestos burned in a current of oxygen prior to using.

A sample of one-half factor weight properly prepared and weighed is placed in the alundum boat, RR Alundum protection being used, and then inserted in the furnace. The stopcock C is opened, and if the furnace is at 950°–1100° C. or over, and the sample of drillings fine and uncovered, it should begin to burn in 20 seconds. The burning should take 40 to 60 seconds additional, consuming 500 ml. of oxygen. An additional 500 ml. of oxygen is turned on to wash out all CO_2, and the bulb is then ready to be weighed.

If the sample is covered by a lid or RR Alundum, or if the drillings are coarse, or the furnace is below 950°–1100° C., the combustion may be delayed as much as two minutes. The actual burning will, as before, take from 40 to 60 seconds. In any event, 500 ml. of gas must be passed through the apparatus after the steel has ceased burning. The point at which the burning of the sample begins may be determined by the increased rate at which gas passes through the liquid in bottle E, due to the rapid absorption of oxygen by the burning steel. A similar decrease marks the end of the burning period.

Standardization of the Stetser and Norton Absorption Bulb.—A freshly filled bulb should be run on the train for half an hour and then weighed. When the bulb has reached a constant weight, the train is checked by running a government standard. By passing the gases from a sample of ignited steel through the bulb, constant weight is more quickly obtained.

A bulb once filled and standardized will last for several weeks and is sufficient for from three to four hundred determinations. On account of the difference in color between the used and unused portions of the absorbent, it is possible to determine the moment a bulb can be discarded.

NOTES.—In chromium, tungsten and titanium steels a temperature of 1500° C. is necessary to oxidize the carbon by direct combustion for thirty minutes. (J. R. Cain and H. E. Cleaves, J. Wash. Acad. Sci., 194, 4, 393–397.)

In the illustration, Fig. 27, the CO_2 passes into the top of the absorption bulb M. It is advisable to have the gas enter at the side arm and pass up through the ascarite and finally through a top layer of anhydrone.

THE SHIMER COMBUSTION APPARATUS [4]

The apparatus, Fig. 28, designed for the rapid determination of iron and steel, is in general applicable to the same class of chemical operations as is the combustion tube of platinum, silica, or porcelain. It offers the advantage of neatness, reduction in the number of parts to be handled, diminished consumption of gas, and increased ease of manipulation. The simplified form, shown in the cut, Fig. 28, enables the use of the standard form of platinum crucible, *A*, with its inner wall ground to fit a tapered nickel, water-jacketed stopper, *B*. The rubber jacket of the original type is eliminated and a detachable nickel reinforcing ring, *C*, at the top of the crucible serves the double purpose of completing the security of the seal and as a support for the apparatus.

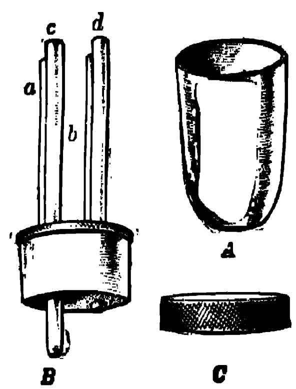


FIG. 28.—Shimer Combustion Apparatus, Simplified Form.

Water is circulated through the stopper through the tubes *c* and *d*. The current of oxygen passes through *a* into the crucible, oxidizing the material within the crucible, which is heated to red heat with a burner placed below it. The carbon dioxide formed passes through *b* to the absorption train. The remainder of the apparatus for the determination is the same as is used with the combustion tube. An asbestos shield protects the upper portion of the outfit, the crucible fitting snugly in a hole in the asbestos board.

COMBINED CARBON

Indirect Method.—The excess of carbon remaining when the graphitic carbon is subtracted from total carbon (in iron and steel), is calculated as combined carbon. This difference method is generally accepted as being the most accurate for estimation of combined carbon.

[4] Courtesy of Baker Platinum Works.

GRAPHITIC CARBON

In Iron and Steel.—The sample of 1 gram of pig iron or 10 grams of steel is treated with 15 ml. of nitric acid (sp.gr. 1.2), per gram of sample taken. When all the iron has dissolved, the graphite is allowed to settle and the supernatant liquid decanted onto an ignited asbestos filter, using either a perforated boat, Fig. 29, or a filtering tube. The residue is transferred to the filter, and washed thoroughly with hot water. It is treated with hot caustic solution (sp.gr., 1.1), washed thoroughly again with hot water, then with a little dilute hydrochloric acid, and finally with hot water. The carbon is now burned by one of the procedures outlined.

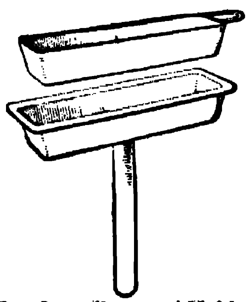


FIG. 29.—Boat and Holder for Carbon Determination.

DIRECT COLORIMETRIC METHOD FOR DETERMINATION OF COMBINED CARBON

The procedure is of value to the steel laboratory where a large number of daily determinations of combined carbon are required. By this method over a hundred determinations a day may be made by an experienced manipulator. The method depends upon the color produced by combined carbon dissolved in nitric acid, the depth of color increasing with the combined carbon content of the material. Comparison is made with a standard sample of iron or steel, which is of the same kind and in the same physical condition as the material tested.[5] That is to say, a Bessemer steel should be compared with a Bessemer standard, open hearth with open hearth, crucible steel with crucible steel, the standards containing approximately the same amounts of carbon, and as nearly as possible the same chemical composition. The samples should be taken from the original bar which has not been reheated, hammered, or rolled. Copper, cobalt, and chromium will interfere with the test; the other elements have very little effect.

Procedure.—One standard sample of 0.2 gram to 1 gram, depending on the carbon content of the steel, and the same amount of sample drillings are taken for analysis. The weighings are conveniently made in brass or aluminum pans, boat-shaped to enable the drillings to be dumped into test-tubes. A counterpoise, weighing the same as the boat, is placed on the opposite pan, together with the 0.2 gram weight. A magnetized knife will assist in removing the excess of material. The weighed sample is brushed into a test-tube 6 in. long (150 mm.) $\frac{5}{8}$ in. (16 mm.) in diameter. (Each test-tube has a label near the open end to distinguish the sample.) A rack or a 600-ml. beaker may be employed for holding the test-tubes during the weighing. After the batch is ready the tubes are transferred to a perforated rack (Figs. 30 or 31) and this then stood in the water bath filled with cold water.

[5] Blair, "The Chemical Analysis of Iron."

The proper amount of nitric acid (sp.gr. 1.2; e.g., 1 conc. HNO_3 : 1 H_2O), from a burette, is now added to each test-tube.

3 ml. HNO_3 for 0.3% C.
4 ml. HNO_3 for 0.3 to 0.5% C.
5 ml. HNO_3 for 0.5 to 0.8% C.
6 ml. HNO_3 for 0.8 to 1% C.
7 ml. HNO_3 for over 1% C. steel.

The depth of color produced by the acid will give an idea of the amount required. One ml. of acid is added at a time until the depth of color is correct. This requires experience gained from observation of the color produced by standard samples. The acid is added slowly to the coarse drillings. Insufficient acid gives a darker tinted solution than it properly should be. The nitric acid should be free from chlorine and hydrochloric acid, since these produce a yellow color. (Cl and $FeCl_3$ are yellow.)

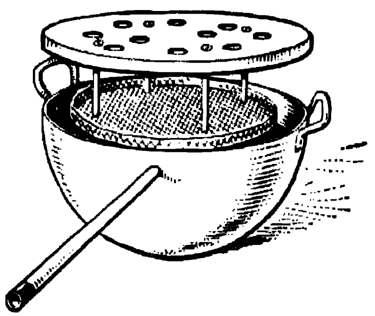


FIG. 30.—Hot Water Racks for Test Tubes.

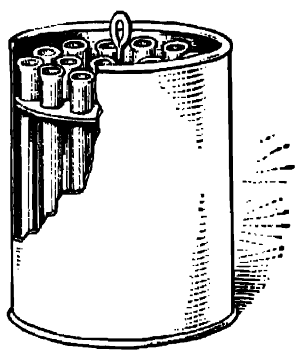


FIG. 31.—Color Carbon Determination.

A glass bulb or a small funnel is placed in each test-tube and the water in the bath then heated to boiling and boiled until all the carbonaceous matter has dissolved, the tubes being shaken from time to time to prevent formation of a film of oxide. Low-carbon steels require about twenty minutes, whereas steels of over 1% carbon require about forty-five minutes. (Blair.) As soon as the bubbles cease and the brownish flocculent matter disappears, the rack is removed from the bath and placed in a casserole of cold water. (Prolonged heating and strong light each causes fading of the color due to combined carbon.)

Color Comparison.—This is made in graduated, clear, colorless, glass cylinders called carbon tubes. The form shown in Fig. 32 was found by W. W. Scott to be the most satisfactory type for a steel-works laboratory where rapidity of manipulation was essential. The bend at the upper portion of the tube facilitates mixing of the solution upon dilution with water, the tube being tilted back and forth until the solution is homogeneous, the bend preventing the liquid from spilling. The dilution should be at least twice that of the amount of nitric acid used, as this amount of water is necessary to destroy the color due to ferric nitrate.

The standard is poured into the carbon tube and the rinsings from the test-tube added. The solution is diluted to a convenient multiple in ml. of the carbon content. For example, 0.45% carbon sample may be diluted to 9 ml.,

then each ml. will represent 0.05% carbon. The sample is placed in a second tube of exactly the same diameter, wall thickness, and form. If the solution of the sample is darker than the standard, water is added little by little, followed by mixing, until the shade matches the standard. If the standard, on the other hand, is darker than the sample, a greater dilution of the standard is necessary, the ml. again representing a multiple of the carbon content. For example dilution of the .45% carbon sample to 15 ml. makes each ml. to represent 0.03 carbon. (It is frequently advisable to take a standard of lower carbon content in place of greater dilution of the standard.)

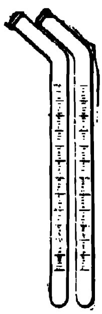


FIG. 32.—Carbon Tubes.

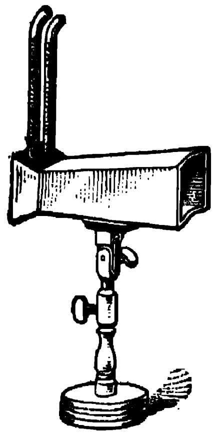


FIG. 33.—Color Comparator or Camera.

Example.—Suppose in the first case the dilution of the sample was 15 ml. in order to match the standard, then $15 \times 0.05 = 0.75\%$ carbon. Six ml. dilution case $2 = 6 \times 0.03 = 0.18\%$ carbon.

The color comparison can be best made in a "camera," a long box with one end closed by a ground-glass screen, Fig. 33. Parallel to the screen and near it, two holes through the top of the box admit the test-tubes. The inner walls of the camera are blackened to prevent reflection of light. If a camera is not available, the tubes may be held side by side and compared against a sheet of white paper held as a background.

BENEKER'S MODIFICATION OF EGGERTZ'S METHOD FOR DETERMINING CARBON IN STEEL

By this procedure interference of the color due to iron is eliminated.

.2 g. of the sample and standard (which does not need to be very similar in carbon content to the sample) are weighed into two test tubes, treated with .7 ml. — 10 ml. of nitric acid of the usual dilution, say 3 parts water to 2 parts acid, and warmed until dissolved and perfectly clear. When cold, ½ ml. of 85% phosphoric acid is added to each tube, transferred to the comparison tubes and read. When this method is used on low carbon steel the bleaching action is very pronounced, because in that case the iron color bleached

out represents the major part of the original color. Dilution of standard or sample introduces no error, because of the absence of the interfering iron color.

ANALYSIS OF GRAPHITE

DETERMINATION OF CARBON

The procedure for determining carbon in graphite is the same as that described for determination of carbon in difficultly combustible organic substances.

The material is broken down in a steel mortar and powdered in an agate mortar. About 0.2 gram is taken for the determination and mixed with copper oxide to assist the combustion, then placed in the boat and the combustion of the carbon carried on according to the standard method in the combustion tube.

$$CO_2 \times 0.2729 = C.$$

DETERMINATION OF CARBON DIOXIDE IN CARBONATES

The method is applicable for determination of carbon dioxide in limestone, dolomite, magnesite, strontianite, witherite, spathic iron ore, carbonates of sodium, and potassium, bicarbonates in baking powder, carbon in materials readily oxidized to CO_2 by chromic sulfuric acid mixture. The procedure depends upon the evolution of carbon dioxide by a less volatile acid, or the oxidation of carbon. The CO_2 is absorbed in caustic and weighed.

Apparatus.—The illustration shows the apparatus found suitable for this determination. It is Knorr's apparatus slightly modified. The absorption bulb or bottle should be one that will effectively absorb carbon dioxide entering at a rapid rate. The Vanier or the Fleming forms are satisfactory for this purpose. Magnesium perchlorate trihydrate may be used in place of P_2O_5 and $CaCl_2$ for drying agent, and soda asbestos in place of soda lime for absorbing CO_2.

Procedure.—A sample weighing 0.5 to 2 grams, according to the carbon dioxide content, is placed in the dry decomposition flask (C). The flask is

closed by inserting the funnel tube (*B*) fitted with the soda lime tube (*A*), and connected by means of a condenser to the train for removing impurities from carbon dioxide, leading to the absorption bulb, as shown in Fig. 34.

The apparatus is swept out with a current of dry, purified air before attaching the weighed absorption bottle. This is accomplished by applying gentle suction at the end of the purifying train. The absorption apparatus is

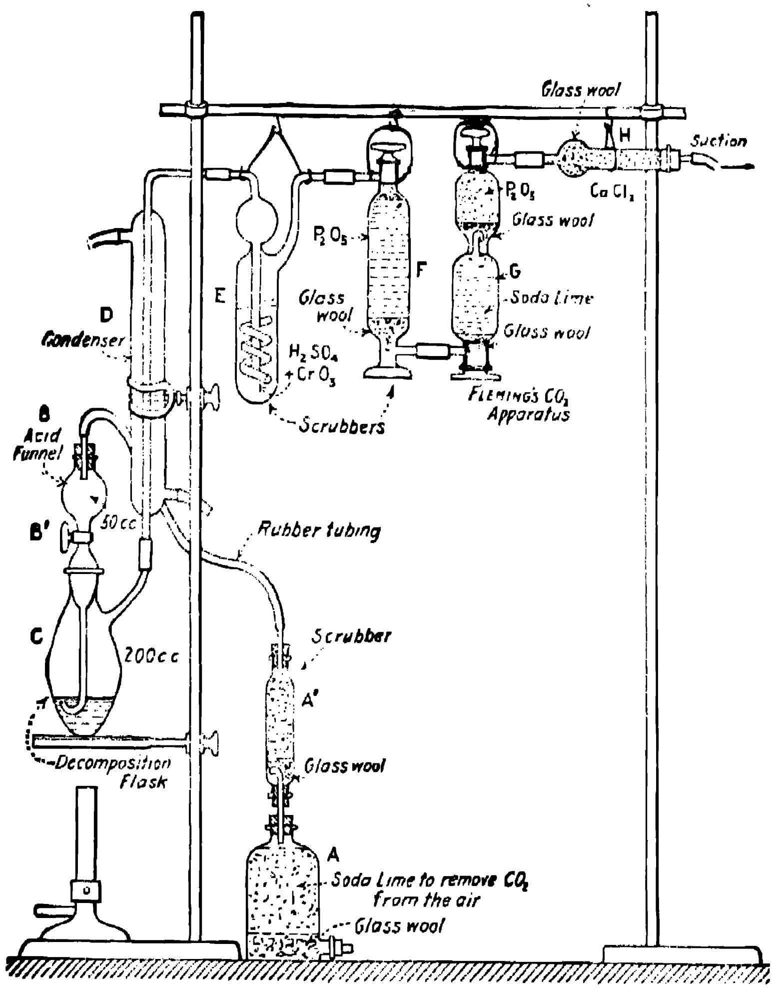


Fig. 34.—Apparatus for Determining Carbon Dioxide.

now attached (Fleming absorption apparatus is shown in the illustration). The tube (*B*) is nearly filled with dilute sulfuric acid (1 : 3), the stop-cock (*B'*) being closed. The soda lime tube is now inserted into place as shown in the cut. The acid in (*B*) is now allowed to run slowly down on the sample at a rate that evolves gas not too rapidly to be absorbed; 1 to 2 ml. of acid being retained in (*B*) to act as a seal, the stop-cock (*B'*) being then closed.

When the violent action has ceased, the solution in (C) is heated to boiling and boiled for about three minutes. If the sample is baking powder, or contains organic matter, the decomposition flask is protected from excessive heat by placing a casserole of hot water under it. This prevents charring of the starch or organic matter, which would be apt to occur if the direct flame was used. Gentle suction is now applied to the absorption end of the apparatus and the stop-cock (B') opened, allowing the remainder of the acid to flow into the flask (C) and admitting a current of air, purified by passing through the soda lime in (A). The suction should be gentle at first, and then the speed of the flow increased to the full capacity of the absorption bottle. A fairly rapid current is preferred to the old-time procedure of bubbling the gas through the apparatus at a snail-like pace, but discretion should be used in avoiding a too rapid flow.

In the analysis of baking powders, where foaming is apt to occur, the decomposition flask should be of sufficient capacity to prevent foaming over. A small flask is generally to be preferred for obvious reasons. By gently heating to boiling during the passage of the air, steam assists in expelling any residual CO_2 in the flask. When the passage of air is rapid, this boiling should be discontinued.

The increase of weight of the absorption bottle is due to the carbon dioxide of the sample. This procedure gives total CO_2.

RESIDUAL CARBON DIOXIDE

This is the CO_2 remaining after baking powder has been treated with water and the evolved CO_2 expelled by warming.

The procedure recommended by the U. S. Department of Agriculture is as follows:[6]

Weigh 2 grams of baking powder into a flask suitable for the subsequent determination of carbonic acid, add 20 ml. of cold water, and allow to stand twenty minutes. Place the flask in a metal drying cell surrounded by boiling water and heat, with occasional shaking, for twenty minutes.

To complete the reaction and drive off the last traces of gas from the semi-solid mass, heat quickly to boiling and boil for one minute. Aspirate until the air in the flask is thoroughly changed, and determine the residual carbon dioxide by absorption, as described under total carbonic acid.

The process described, based on the methods of McGill and Catlin, imitate, as far as practicable, the conditions encountered in baking, but in such a manner that concordant results may be readily obtained on the same sample, and comparable results on different samples.

AVAILABLE CARBON DIOXIDE

The residual is subtracted from the total, and the difference taken as available CO_2.

DETERMINATION OF CARBON DIOXIDE BY LOSS OF WEIGHT

An approximate estimation of the carbon dioxide in carbonates—baking powders, bicarbonate of soda, limestone, etc., may be obtained by the loss of weight of the material when treated with a known weight of acid.

[6] Bureau of Chem. Bulletin No. 107.

Various forms of apparatus are used for this determination. The Schroetter and Mohr types are shown, Figs. 35 and 36.

About 0.5 to 1.0 gram of sample is taken and placed in the bottom of the flask, dilute hydrochloric and conc. sulfuric acids then placed in the bulbs as indicated in the illustrations. The apparatus is weighed as it is thus charged. The hydrochloric acid is now allowed to flow down on the carbonate and the

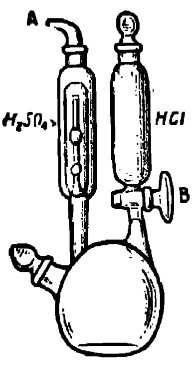


FIG. 35.—Schroetter's Alkalimeter.

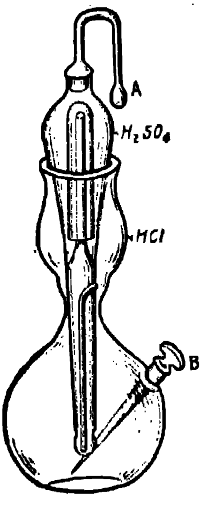


FIG. 36.—Mohr's Alkalimeter.

stopper closed. The evolved gas passes through the conc. sulfuric acid, which absorbs the moisture. After the vigorous action has subsided the apparatus is placed over a low flame and the solution heated to boiling and boiled very gently for about three minutes. CO_2-free air is aspirated through the solution to expel the last traces of CO_2, by applying gentle suction at *a* and opening *b*, the air being purified by passing through soda lime. The apparatus is again weighed and the loss of weight taken as the CO_2 of the material.

Available CO_2 in baking powder may be determined by substituting water in place of hydrochloric acid.

LOSS OF WEIGHT METHOD FOR CARBON DIOXIDE DETERMINATION IN CARBONATES[7]

Apparatus.—An Erlenmeyer flask of 50 ml. capacity, Fig. 36A, is fitted with a two hole rubber stopper bearing a short calcium chloride tube, filled with calcium chloride of about 16 mesh granules. The tube is best prepared by cutting down a regular sized tube so that its length over all will be not over 3″. The upper end of the calcium chloride tube is fitted with a one hole rubber stopper through which passes a short glass tube, bent at right angles as shown in the drawing. This tube is closed with a rubber tip of a policeman rod. The other hole of the two hole stopper is fitted with a glass tube passing through the

[7] Wilfred W. Scott and Paul W. Jewell, Ind. Eng. Chem., Anal. Ed. 2, 76 (1930).

stopper to the bottom of the flask, the lower end drawn to a capillary point. The upper end is bent as shown in the drawing. The upper end is also closed with a rubber policeman tip.

The purification train consists of a fairly large "U" tube, the arm next to the apparatus is filled with calcium chloride, and the other is filled with soda lime. The air as it enters the apparatus is drawn through this train and is thus freed from moisture and carbon dioxide.

Determination.—When the apparatus is assembled, a volume of about 15 ml. of dilute hydrochloric acid, 1 : 1, is placed in the flask and the apparatus weighed. About 0.5 g. sample is placed in a weighed glass thimble, consisting of a two dram homeopathic vial, the upper part cut off so that one inch remains, the edge being fire dressed. The sample is now weighed. (Weight of vial and sample minus weight of vial.) The thimble and sample are carefully introduced in the flask by means of tweezers, being careful not to upset the vial. The weight of the entire apparatus, thimble and sample are now known. The apparatus is closed by replacing the stopper. The rubber policeman tip from the exit calcium chloride tube is removed. The thimble is overturned by agitating the apparatus. When the action has subsided the apparatus is attached to the purification train (the inlet policeman tip having been removed). Suction is applied so that the bubbles pass through the apparatus at the rate of about two per second. At this rate the aspiration is continued for fifteen minutes. The purification train is now detached, the policeman tips replaced on the apparatus, and the entire apparatus weighed.

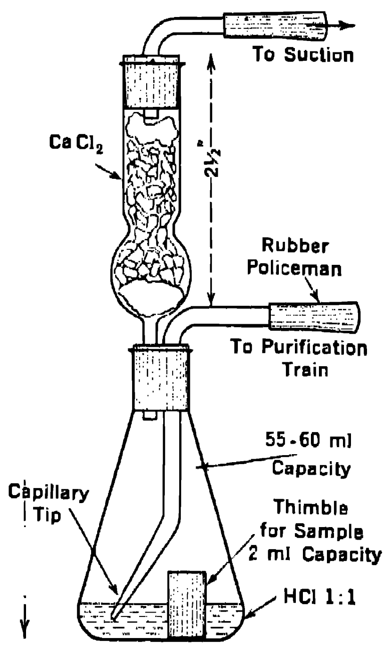


Fig. 36A.—Apparatus for Determining Carbon Dioxide by loss in weight.

The loss of weight is due to the escape of carbon dioxide.

$$\frac{\text{Loss of Weight} \times 100}{\text{Weight of Sample}} = \% \ CO_2.$$

Notes.—The method is accurate to 0.1%.

The calcium chloride should be replaced after about ten determinations. Dehydrite will last longer (about 25 determinations) but should this be used in place of calcium chloride, it must also be used in the purification train.

It is well to start with a sample of pure $CaCO_3$ to become familiar with the procedure. CO_2 in $CaCO_3$ is 44%. Run an "unknown" following the "known."

In cutting the vial or the calcium chloride tube make a short sharp scratch on the tube where the cut is to be made using a file. Now heat the edge of the file to redness and hold against the scratch. The tube will generally break off squarely at the cut.

DETERMINATION OF CARBON DIOXIDE BY MEASUREMENT OF THE GAS[8]

Determine carbon dioxide on a 0.2 gram sample of the limestone, using the apparatus and procedure described below Fig. 36B.

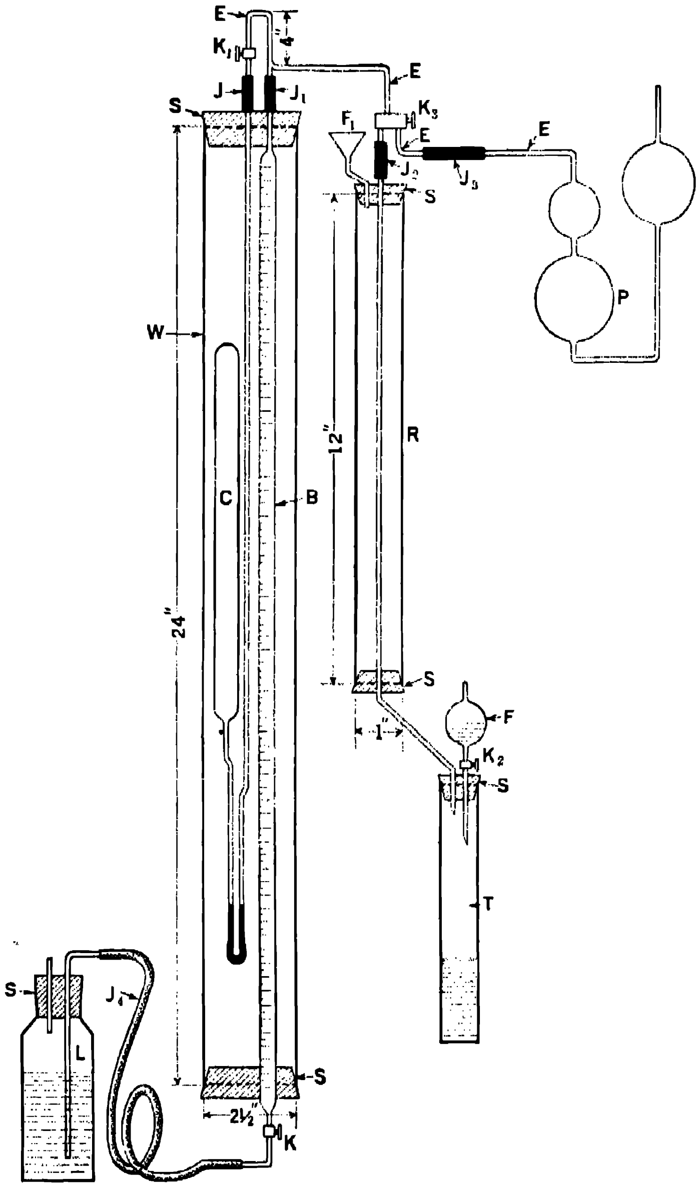


FIG. 36B.—Determination of Carbon Dioxide by measurement of the volume.

[8] Standard Method for Determining CO_2 in Limestone of the Solvay Process Company. By courtesy of this Company.

Apparatus.—The various parts of the apparatus are designated on the diagram as follows:

B = 100 ml. gas burette, modified at top as shown.
C = Compensator tube, made conveniently from a 20-ml. pipette. The chamber contains Hg as indicated in the light section. This tube is small but not a capillary.
W = Water jacket enclosing "B" and "C."
J, J_1, J_2, J_3 = Strong rubber connections. The glass tubes from J to J_1 and J_1 to J_2 are capillary. The tube from J_2 to receptacle is 5 mm. glass tubing.
K, K_1, K_2, and K_3 = Stop cocks. K_3 is a three-way cock.
L = Leveling bottle for the burette (connected by rubber tubing).
R = Condenser. Usually this needs only to be filled with water, not to have water running through it.
F = Funnel for introducing acid.
P = Caustic potash pipette, which contains beads to expedite the CO_2 absorption.
T = Receptacle for sample. A test tube when sample is 20 ml. or under, a small flask when sample is larger.

Operation.—In T place a small piece of iron wire (larger than a pin head), a drop of methyl orange and the sample to be tested. If the sample is solid, add enough water to make the volume at least 10 ml.

Level the Hg columns, close cock K_1, fill the burette with water and close cock K. Connect T and close cock K_2. Pour an excess of concentrated HCl into F.

Now open cock K fully and K_2 sufficiently to let the acid drop slowly into T until very slightly in excess. Close K_2, fill F nearly full with water, heat the contents of T to boiling and continue boiling very gently for at least 2 minutes. Remove the burner, open K_2 immediately and lower L (if necessary) until the water from F fills T and the connecting tube up to J_2. Give three-way cock K_3 one-quarter turn to cut off all openings. Raise L until its water is approximately at the same level as the water in the burette, open K_1, and raise or lower L until the two mercury columns are level; then close K and K_1, set L down and read burette.

Next turn K_3 to connect with potash pipette P and run gas over into the pipette and back again repeatedly until CO_2 is absorbed (three times should suffice). After finally returning the gas to the burette, close K_3, level the mercury columns and read the burette in the same manner as before.

Calculation.—The difference between the two burette readings, multiplied by a definite factor (for the determination of which see the following paragraph), gives the weight of carbon dioxide (CO_2) present in the sample.

$$\frac{\text{Ml. of } CO_2 \times \text{factor} \times 100}{\text{Wt. of Sample used in Evolution}} = \%\ CO_2.$$

Determination of Factor.—The factor may be determined theoretically, but more conveniently by a series of actual tests on a sample of known CO_2 content. It is recommended that the C.P. sodium carbonate for acidimetric standard be used. Weigh accurately exactly 2 grams of the sodium carbonate, dissolve in

25 ml. of distilled water free from carbon dioxide, and transfer to a standard 100 ml. measuring flask. Cool to 20° C., dilute to the mark with distilled water free from carbon dioxide, and mix thoroughly. Use 10 ml. aliquot portions of this, measured by means of a standard pipette, in determining the amount of carbon dioxide (CO_2) it contains by the evolution method. The factor is calculated by substitution in the following formula:

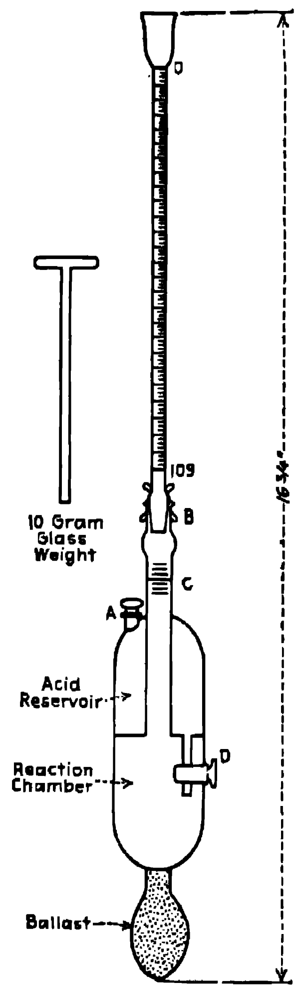


FIG. 37.—Barker's Hydrometer.

$$\text{Factor} = \frac{\%\ Na_2CO_3 \text{ in the material used} \times 0.2}{\text{Ml. of carbon dioxide} \times 240.91}.$$

Remarks.—The time required for a test is from 5 to 10 minutes after the sample is introduced into T.

In the original adjustment of the mercury columns in the compensator it is preferable to manipulate so that the columns are about level under the ordinary atmospheric pressure and temperature of the laboratory.

The use of a conc. NaCl or $CaCl_2$ solution in place of water in the burette is perhaps advisable for accurate work, though water has been found very satisfactory.

DETERMINATION OF CO_2 IN CARBONATES—HYDROMETER METHOD OF BARKER[9]

No mechanical balance or scale is required by the following procedure.

The method depends upon the principle of the hydrometer, following the law that when an object is immersed in a liquid it is buoyed up by a force equal to the weight of the liquid displaced by the object. The carbon dioxide set free from the sample decreases the weight; and the rise of the graduation scale tube above the water records the percentage of carbonates from which the gas was released. The procedure is suitable for determining the comparative strengths of baking powders, for rapid tests of the quality of limestone and for estimation of carbon dioxide of carbonates in general.

Procedure.—To analyze a sample for carbonates measure out 40 ml. of hydrochloric acid (sp.gr. 1.15), using a small graduate; pour this into the acid reservoir through the opening *A*. With graduated stem disconnected hang a 10 gram weight at *B*. The hydrometer should then float in a cylinder of water and be immersed to some point at *C*. Remove the 10 gram weight and introduce pulverized limestone, or other substance that is being tested, until the

[9] J. F. Barker, J. Ind. Eng. Chem., 9, 786–787, 1917.

instrument is immersed to exactly the same point that it occupied with the suspended weight. The reservoir will now contain 10 grams of sample. Connect up the graduated stem and add water, a drop at a time, through the funnel-shaped top, until immersed to the zero point. Raise the hydrometer out of the water and open the stopcock *D* until the acid drops slowly into the reaction chamber, decomposing the carbonate. As the reaction proceeds the instrument rises slowly and at the conclusion the point on stem at the surface of the water gives the per cent of calcium carbonate equivalent to the carbon dioxide in the sample. This figure is the calcium carbonate equivalent so often mentioned in connection with limestone analyses.

A Fahrenheit thermometer accompanies each instrument and is hung inside the floating cylinder. Its reading is taken before and after each determination to allow for any error due to change in temperature. To the figure for calcium carbonate equivalent add 0.5 for each degree rise, or subtract 0.5 for each degree fall in temperature between the two readings. This temperature change need seldom amount to more than a fraction of a degree.

NOTES.—The limestone may be weighed to an accuracy of 0.02 gram. The weight of CO_2 remaining in the apparatus tends to offset the loss due to moisture escaping with the gas, but the difference, together with any other sources of error has been accounted for in the graduation of the reading stem.

DETERMINATION OF PERCARBONATES

Percarbonates are decomposed by dilute sulfuric acid according to the reaction $K_2C_2O_6+2H_2SO_4=2KHSO_4+2CO_2+H_2O_2$.

Procedure.—Two-tenths of a gram of the salt is added to about 300 ml. of cold dilute sulfuric acid (1 : 30). The liberated hydrogen peroxide is titrated with potassium permanganate.

$$1 \text{ ml. } N/10 \text{ } KMnO_4 = 0.00991 \text{ g. } K_2C_2O_6.$$

VOLUMETRIC METHODS FOR THE DETERMINATION OF CARBON

TOTAL CARBON. ABSORPTION OF CARBON DIOXIDE IN BARIUM HYDROXIDE

The carbon dioxide evolved by oxidation of the material by dry combustion with oxygen or by oxidation with chromic sulfuric acid mixture is absorbed in barium hydroxide, free from carbonate, and the precipitated barium carbonate titrated with standard hydrochloric acid.

Procedure.—The essential difference in this method from those already described under the gravimetric methods is in the fact that a perfectly clear

saturated solution of barium hydroxide is used for absorption of the carbon dioxide in place of caustic potash. Considerable care must be exercised to prevent contaminating the reagent with carbonate. The solution is drawn by suction through a siphon, dipping below the surface of the reagent, into the absorption tube, which should be of such construction that the material may readily be poured out. Details of the procedure are given in the chapter on Iron and Steel, Volume II, under carbon determination. The precipitate, barium carbonate, is filtered off and washed by a special procedure, and then titrated with standard hydrochloric acid.

$$1 \text{ ml. } 0.1 \text{ N HCl} = 0.0006 \text{ g. carbon}$$

DETERMINATION OF CARBON BY MEASUREMENT OF THE VOLUME OF CARBON DIOXIDE EVOLVED BY OXIDATION OF CARBON, OR BY THE DECOMPOSITION OF CARBONATES WITH ACID

Description of the Scheibler and Dietrich Process and that of Lunge and Marchlewski are given in Mellor's work on "Inorganic Analysis," pp. 555–559, 1st Ed. A modification of Wiborg's method is described in Blair, "Chemical Analysis of Iron," pp. 146–149, 7th Ed.

DETERMINATION OF CARBON DIOXIDE IN A GAS MIXTURE

See Gas Analysis.

CERIUM AND THE RARE-EARTH ELEMENTS [1]

The rare-earth group of elements is commonly taken to mean those elements lying between, and including, lanthanum, of atomic number 57, and lutecium, of atomic number 71, as well as the element yttrium, of atomic number 39. For the sake of convenience the elements are divided into three sub-groups:

Cerium Group			Terbium Group			Yttrium Group		
	At. No.	At. Wt.		At. No.	At. Wt.		At. No.	At. Wt.
Lanthanum (La) ..	57	138.92	Europium (Eu)	63	152.0	Dysprosium (Dy)	66	162.46
Cerium (Ce)	58	140.13	Gadolinium (Gd)	64	156.9	Holmium (Ho).	67	163.5
Praseodymium (Pr)	59	140.92	Terbium (Tb).	65	159.2	Yttrium (Y) ..	39[2]	88.92
Neodymium (Nd) .	60	144.27				Erbium (Er)...	68	167.64
Illinium (Il).......	61	Not det.				Thullium (Tm)	69	169.4
Samarium (Sm) ...	62	150.43				Ytterbium (Yb)	70	173.04
						Lutecium (Lu)	71	175.0

This division is somewhat arbitrary, and the lines of demarcation are not sharp. The most definite indication of a distinct difference is found in the platinocyanides, $R_2Pt(CN)_{12}$, those of the cerium group being yellow monoclinic crystals with 18 H_2O, while those of the terbium and yttrium groups form red rhombic crystals with 21 H_2O. The members of the cerium and terbium groups differ from those of the yttrium group by forming double nitrates with many uni- and di-valent elements. A difference of importance from the analytical standpoint is the variation in the solubilities of the double potassium or sodium rare-earth sulfates in concentrated solutions of potassium or sodium sulfate, those of the cerium group being very difficultly soluble and those of the yttrium group being rather readily soluble, while the members of the terbium group occupy an intermediate position. But even this difference in solubility should be considered as a variation from element to element rather than as a definite variation from group to group. The order of increasing atomic numbers is often spoken of as the "Serial Order" of the rare-earth elements, for the basic strengths of these elements become progressively weaker in this order, and the solubilities of most salts vary in the same order, either directly or inversely. These variations in solubility, very slight as they are, are of tremendous importance, for the chemical reactions of all the rare-earth elements are so strikingly similar that, with the exception of cerium and europium, no rare-earth element can be separated from the others by the use of any specific precipitant so far discovered, and in general it is only by tedious

[1] Paul H. M.-P. Brinton, Ph.D., Consulting Chemist, Visiting Professor University of Southern California, Los Angeles, Calif.

[2] The inclusion of the apparent "outsider," yttrium, in this position cannot be discussed here. See Brinton and James, J. Am. Chem. Soc., 43, 1446, 1921.

processes of fractional crystallization or fractional precipitation that one of these elements can be obtained in a state of even approximate purity.

The distribution of the rare-earth elements in the earth's crust is reasonably wide, and small amounts may be found in many rocks. The most important[3] minerals containing notable amounts of them may be classified in three groups.

(a) **Silicates.**—Gadolinite contains iron, beryllium and members of the yttrium group, with small amounts of the cerium and terbium groups. Cerite consists mainly of the silicates of the cerium group. Allanite, of which there are several varieties carrying special names, contains principally calcium, iron, aluminum and the cerium earths.

(b) **Phosphates.**—Monazite sand, the most important commercial source of cerium, is essentially an orthophosphate of the cerium earths, but carries small amounts of the other earths, and is likewise the source of most of the thorium that comes into the market. Monazite occurs largely in Brazil, India and South Carolina. Xenotime is an orthophosphate of the yttrium earths.

(c) **Tantalates and Columbates.**—Fergusonite is a tantalate and columbate of the yttrium earths, with varying amounts (often reasonably large) of cerium and terbium group members. Euxenite is a columbo-titanate of the yttrium group, with small amounts of the cerium group, and considerable uranium. Samarskite, a columbotantalate of yttrium, iron and calcium, is also rich in uranium, and forms one of the best sources of the terbium group.

The industrial applications of the rare-earth elements are quite limited, although cerium is really of some commercial importance. Incandescent gas mantles contains about 1% of cerium dioxide (the rest being mainly thorium dioxide). The pyrophoric alloy used in lighters is essentially an alloy of iron and cerium, and the so-called "mischmetall" used in metallurgical reductions is a mixture of the metals of the cerium group. In ceramics the use of the rare-earth elements is increasing, and the members of the cerium group are used in optical glass to give protection to the eyes from the ultraviolet rays, which are largely absorbed by the transparent solutions of these elements. Ceric sulfate is now widely used as a standard volumetric solution in oxidimetric analyses. See the Chapter on Reagents, Section III. Various other uses for rare-earths have been suggested, but the importance of these applications scarcely justifies detailed description.

The quantitative determination of the total rare-earths in a sample is an analytical problem of no very great difficulty, whereas the qualitative detection of the individuals which make up the total is a task which presents great difficulties. Since the procedure for the detection of the presence of rare-earths is essentially the same as for their quantitative estimation as a group, it seems scarcely worth while going through the process without weighing the initial sample and the final product.[4] Moreover, success in the qualitative

[3] For a fuller discussion of rare-earth minerals and occurrences see H. F. V. Little in vol. IV of Friend's Textbook of Inorganic Chemistry; vol. V of Mellor's Treatise on Inorganic and Theoretical Chemistry; and vol. VI, Part 1, of Gmelin-Kraut's Handbuch der anorganischen Chemie.

[4] Of course, if we have an ammonium hydroxide group precipitate in which we are certain that all the rare-earths of the original sample are contained, and if the absence of phosphates, thorium and scandium are assured, the detection of rare-earths is easily accomplished by solution in acid and precipitation by oxalic acid. Unfortunately, however, such simplifying assumptions are rarely justified.

detection of these elements is dependent in no small degree upon the decomposition of the original sample, especially if it be a mineral, and the subject of decomposition must be somewhat fully treated in connection with the quantitative determination, so it seems best to vary a little for this chapter the order of procedure followed in the rest of the book, and to discuss first the simpler problem of the quantitative determination of total rare-earth oxides, and then to proceed to the more intricate problem of trying to find out which elements go to make up that total.[5] In a few instances a fair idea of the approximate amounts of the various constituents can be obtained, but this cannot be done in all cases without an expenditure of time and effort which is not usually commensurate with the benefits to be derived from such information.

QUANTITATIVE DETERMINATION OF TOTAL RARE-EARTHS

Decomposition of the Sample.—The silicates, such as gadolinite and cerite, if very finely ground, can be fully decomposed by concentrated hydrochloric acid by long digestion in a covered vessel, more acid being from time to time added if it seems necessary. If hard, non-gelatinous particles persist, the residue should be fused with sodium or potassium pyrosulfate, taken up with dilute acid, and added to the main portion. Silica is then to be removed by evaporation in the regular way. Concentrated sulfuric acid is also a good solvent for the rare-earths in these silicates, and if the decomposition requires a somewhat longer treatment than is needed with hydrochloric acid, this is perhaps offset by not having to evaporate to render the silica insoluble.

Phosphates, such as monazite, are best decomposed by long treatment with concentrated sulfuric acid at a temperature which keeps fumes of sulfur trioxide in gentle evolution. For details see the decomposition of monazite in the chapter on Thorium, and note that sufficient acid must be present at the end of the digestion to prevent the separation of rare-earth phosphates on dilution.

Tantalates, columbates and titanates, such as fergusonite, euxenite and samarskite are not as a rule sufficiently fully decomposed by treatment with hydrochloric or sulfuric acid for exact analytical procedures, though such treatment may frequently serve for the larger scale extraction of rare-earths for preparative purposes. Fusion with sodium [6] pyrosulfate will decompose these

[5] Simple qualitative tests for the presence or absence of the rare-earth group as a whole, without respect to individuals, are indicated in foot-notes to the quantitative procedure for total rare-earths.

[6] Potassium pyrosulfate may be used, though it is less advisable, since the cerium group double potassium sulfates are less soluble in the presence of potassium sulfate than are the corresponding sodium salts in the presence of sodium sulfate. If the potassium salt is used greater care must be taken to insure the complete extraction of the melt.

minerals if they are finely ground and fused for about an hour with six times their weight of flux, occasionally cooling sufficiently to allow the addition of a few drops of sulfuric acid. On treatment with cold water—care being taken to prevent undue rise in temperature, which diminishes the solubility of the rare-earth sulfates—silica, tantalic and columbic acids remain, while the rare-earth sulfates pass into solution. Samarskite, fergusonite, and similar minerals can also be conveniently brought into solution by hydrofluoric acid. The finely divided sample is covered with hydrofluoric acid [7] in a platinum dish and heated very gently, occasionally stirring with a stout platinum wire, until all dark particles have been brought into solution. The mixture is evaporated until only a few ml. of liquid remain, and it is then diluted with 50 ml. of water and allowed to stand several hours. The rare-earth fluorides, together with the fluorides of scandium, thorium and any quadrivalent uranium, are almost quantitatively insoluble, while the fluorides of the other elements, including tantalum and columbium, remain in solution. Alkaline earth fluorides will, however, be divided between the precipitate and the solution. The precipitate is filtered on paper in a hard rubber funnel and washed with dilute hydrofluoric acid. The fluoride precipitate is rinsed into a platinum dish and the paper is ignited and added to the contents of the dish. The fluorides are evaporated with sulfuric acid to copious fumes of sulfur trioxide, and, after cooling, the residue is taken up in water. Any small amounts of tantalic and columbic acids would be insoluble, and are to be filtered off. Precipitation by ammonium hydroxide will free the tri- and quadrivalent elements from alkaline earths. If the highest accuracy is desired the fluoride solution, containing the bulk of the tantalum and columbium must be evaporated with sulfuric acid, filtered, and in the filtrate the minute quantity of rare-earths which was soluble in hydrofluoric acid is precipitated with oxalic acid, ignited to oxide, dissolved in acid and added to the main portion.

Separation of the Rare-Earths from Phosphoric Acid.—The rare-earth solution, which should contain about 5% of its volume of nitric or hydrochloric acid, and which has been freed from heavy metals by hydrogen sulfide in the conventional manner, is poured into a hot solution of 10 g. of oxalic acid, and well stirred. After standing some hours the oxalates are filtered,[8] washed with water containing a little hydrochloric and oxalic acids, ignited to oxide, dissolved in dilute hydrochloric acid,[9] and the precipitation as oxalate is repeated just as before. Two precipitations as oxalate suffice to remove practically all the phosphates, but if the very highest accuracy is desired a third precipitation with oxalate would be advisable. The final oxalate precipitate contains only rare-earths, scandium and thorium.[10]

[7] In the case of silicates, or samples high in silica, it is well to add a little water to the powder, and then only a few ml. of hydrofluoric acid. After the vigorous action is over the rest of the acid may be added.

[8] Failure to get a precipitate here is, of course, proof of the absence of rare-earths in the sample.

[9] If one is interested in knowing just whether any rare-earths are present in the sample, qualitative proof of their presence can usually be obtained from this solution, for it is almost certain that any naturally occurring mixture of rare-earths will include some which will give absorption spectra. (See the section on spectroscopic examination of the rare-earths.)

[10] It has been stated by Hauser, Z. anal. Chem., 47, 677, 1908, and Canneri and Fernandes, Gazz. chim. ital., 54, 770, 1924, that in presence of uranium the precipitation

Separation of the Rare-Earths from Scandium and Thorium.—The oxalate precipitate is ignited and then dissolved in as little 1 : 1 hydrochloric acid as possible, warming and allowing sufficient time to insure complete solution. If the percentage of cerium in the mixture is high it may be necessary to use concentrated hydrochloric acid and a few grains of potassium iodide to effect the solution of the oxides. The solution must then be well boiled to expel the free iodine. The solution is largely diluted and treated with ammonium hydroxide until a very faint precipitate persists in spite of vigorous stirring. This turbidity is cleared by the dropwise addition of hydrochloric acid, finally adding just a few drops in excess. The solution, in volume not less than 400 ml., is heated to boiling, and 15 g. of sodium thiosulfate dissolved in 50 ml. of hot water are added and the mixture is gently boiled for an hour. The basic thiosulfates of thorium and scandium are filtered and washed with hot water. The filtrate contains the rare-earths, but the basic thiosulfate still retains appreciable amounts of these elements. So it is redissolved in 1 : 1 hydrochloric acid and the precipitation by sodium thiosulfate is repeated a second and a third time just as before. The combined filtrates contain all the rare-earths, and if the conditions here given (note the absence of nitric acid) are followed not more than traces of thorium, and no scandium, will be in the filtrate. If the thiosulfate precipitation is carried out in a solution not sufficiently diluted, some rare-earths, especially the members of the yttrium group, will be retained with the thorium even after several reprecipitations.

The combined filtrates are evaporated to about half their volume, and any separated sulfur is filtered off, burned in a porcelain crucible, and the slight residue of rare-earths which had been mechanically carried down with the sulfur is dissolved in hydrochloric acid and added to the solution. Ammonium hydroxide is added to the solution in slight excess, and the rare-earth hydroxides are filtered off, washed, and dissolved from the paper in dilute hydrochloric acid. In this solution, which should be hot and contain 3 or 4 ml. of concentrated hydrochloric acid per 100 ml., the rare-earth oxalates are precipitated by adding a hot solution of oxalic acid in generous excess. After standing several hours the oxalates are filtered, washed, and ignited to constant weight [11] over a large Meeker burner in platinum, or over the blast in porcelain. The results are reported in terms of total rare-earth oxides. It must be realized that this represents R_2O_3 for all the earths except cerium, which is CeO_2, praseodymium, Pr_6O_{11}, and terbium, probably Tb_4O_7. Consequently, since these elements all seem to occur in nature in the trivalent form, one would not,

of rare-earths as oxalate is incomplete, and that a part of the uranium is retained in the oxalate precipitate. R. C. Wells, J. Am. Chem. Soc., 50, 1017, 1928, states that at dilutions proper to analytical work no abnormality in the presence of uranium is observed. Preliminary experiments in the writer's laboratory indicate that bright sunlight is best avoided during the separation of rare-earths from uranium as oxalate. Further work is in progress.

[11] There is some uncertainty about the ignition of these oxides in air, as even in the ignition of individuals other than cerium, praseodymium and terbium a tendency of the weight to reach a minimum and then gradually to increase has been noted. (Sarver and Brinton, J. Am. Chem. Soc., 49, 948–950, 1927.) Yet Pagel and Brinton, *ibid.*, 51, 42, 1929, seem to have shown conclusively that the rare-earth elements, with the three exceptions noted, do not tend to form higher oxides. The matter is under further investigation. If this tendency toward increasing weight is found the minimum weight should be taken as the correct one.

of course, expect to reach a summation of 100% in a complete analysis of a mineral if the total rare-earths were reported as here found. It is impossible to reduce the whole to the sesquioxide form by heating in hydrogen, since cerium dioxide is only very slightly reduced by this procedure. The higher oxides of praseodymium and terbium are readily reduced by hydrogen when unaccompanied by cerium, but what would be their behavior when in intimate mixture with much cerium is problematical. If the actual weight of the total rare-earth sesquioxides is desired, the cerium must be separated from the other rare-earths by the iodate method later described, weighed as CeO_2 and calculated to Ce_2O_3. In the filtrate from the basic ceric iodate the other earths are precipitated by sodium hydroxide, dissolved in hydrochloric acid, precipitated as oxalates, and ignited in a Rose crucible until all carbon is burned off. The ignition is then finished by heating over the blast in a current of hydrogen to constant weight. This gives the sesquioxides of all the earths other than cerium.

THE APPROXIMATE DETERMINATION OF THE CERIUM AND YTTRIUM GROUPS

Having obtained the total rare-earth oxides by the procedure just outlined, it is possible to get an approximate determination of the percentage of the total cerium group oxides and of the total yttrium group oxides, based on the difference in the solubilities of the double alkali sulfates of the two groups in saturated solutions of the respective alkali sulfate. The sodium salt in solid form is widely recommended, but the writer prefers to work with the saturated solution of potassium sulfate, which tends less to precipitate the yttrium group, and, if anything, tends to retain neodymium and samarium more completely with the cerium group.

It is well to have as large a sample as possible for this separation, and with less than 0.5 g. of oxides the results are not very trustworthy.[12] Only a small quantity of acid should be present, so if in the form of a chloride or nitrate the solution should be evaporated to approximate dryness, moistened with a drop

[12] Rather than take the total oxides obtained according to the preceding section as the starting point for the potassium sulfate precipitation, it is often better, if the amount of the original material is sufficient, to take a larger sample and make the separation on the oxides obtained from the oxalate precipitation which is made just before the separation from thorium and scandium. Both thorium and scandium will go practically quantitatively into the potassium sulfate. (This is not true of scandium if sodium sulfate is used.) The percentage of thorium oxide will usually have been separately determined by one of the methods given in the chapter on that element, so the weight of ThO_2 can be deducted from the weight of the cerium group oxides. The amount of scandium in any mineral likely to be met is so small that its effect could hardly be significant in a separation no more exact than the one under consideration.

or two of the respective acid, and taken into solution with as little water as possible. If a sulfuric acid solution be present it is more convenient to precipitate with ammonium hydroxide and redissolve in hydrochloric acid than to carry out the tedious expulsion of the excess sulfuric acid at an elevated temperature.

To the cold, concentrated chloride or nitrate solution about 200 ml. of a saturated solution of potassium sulfate are added, and then a few grams of finely powdered potassium sulfate are sifted in, the mixture being vigorously stirred in the meantime, and for some minutes afterwards. After not less than 12 hours the precipitate is filtered and washed twice with saturated potassium sulfate solution, no attempt being made to thoroughly clean the beaker. The filter with the double sulfates is dropped back into the original beaker. The liquid adhering to the funnel is rinsed into the filtrate, and this solution, containing the bulk of the yttrium earths, is temporarily set aside. The first precipitate and paper are boiled with about 100 ml. of 10% sodium hydroxide solution, diluted to about 250 ml., again boiled, filtered and washed. The hydroxides are dissolved in hydrochloric acid, freed from filter paper by filtration, evaporated to approximate dryness, moistened with a drop or two of hydrochloric acid, taken up with a little water, and the sulfate precipitation is repeated just as before. This second precipitate is again treated with sodium hydroxide and hydrochloric acid just as described before. In the resulting chloride solution the cerium earths are precipitated as oxalates and weighed as mixed oxides just as outlined in the method for total rare-earth oxides. The combined filtrates from the double sulfate precipitations are treated with ammonium hydroxide, the resulting yttrium earth hydroxides are dissolved in hydrochloric acid, precipitated as oxalates, ignited to oxides and weighed. In the case of the yttrium earths the use of hydrogen for the ignition would never be necessary in the analysis of any naturally occurring group of earths, for praseodymium is absent, and not more than traces of terbium could be present, owing to the scarcity of this element. It is evident that if no further investigation is to be carried out, the weighing of either the cerium group or the yttrium group would suffice, since the other group could be determined by difference from the percentage of the total oxides already determined.

Under the conditions here outlined the members of the terbium group will be mostly with the cerium earths, and a small amount of the yttrium earths will also be here. On the other hand the yttrium group contains slight amounts of the cerium group, particularly samarium and neodymium. On the whole, however, a fair idea can be had from this separation as to the relative proportions of the two main groups present, and as long as working conditions are maintained reasonably constant, and the amounts worked upon are not too small, fair checks can be obtained in duplicate analyses.

DETERMINATION OF CERIUM

The individual determination [13] of cerium is one of the few processes in the chemistry of the rare-earths which is reasonably exact. It can be separated from all other rare-earths by gravimetric methods, and it can also be accurately determined by volumetric processes without having to separate it from its neighbors.

Gravimetric Determination.—Cerium may be separated from other rare-earths by several processes which accomplish two things, (*a*) the oxidation of cerium to the quadrivalent stage, and (*b*) the promotion of the quantitative hydrolysis of the ceric compound, which is very weakly basic in comparison with the trivalent earths. Hydrogen peroxide and ammonia,[14] chlorine or bromine and sodium hydroxide,[15] potassium permanganate and sodium carbonate,[16] potassium bromate and marble [17] or sodium carbonate,[18] and, finally, trinitratotriamminecobalt [19] as both oxidizer and hydrolytic agent, are among the most satisfactory combinations proposed for the complete separation of cerium from its associated earths. In practice it is difficult to accomplish the complete hydrolysis of cerium without contamination with other earths, and numerous repetitions are generally necessary before complete separation is attained. The trinitratotriamminecobalt method is said to accomplish the separation in one operation, even though that operation is a somewhat long one. Nevertheless, since it requires a reagent which is not always readily available it must suffice here to cite the reference.

Potassium iodate [20] is the only specific precipitant which has been proposed that is not dependent upon hydrolysis, and it offers a ready means of separating cerium quantitatively from even large amounts of other rare-earths. Thorium, if not previously removed, would be quantitatively precipitated along with the cerium. Moreover it is entirely justifiable to make a separate determination of the thorium by one of the specific methods given for that element in the chapter on Thorium, and then deduct the weight of ThO_2 from the combined weight of the cerium and thorium oxides found.

To the solution containing the rare-earth nitrates (thorium having been previously removed) is added enough concentrated nitric acid so that the latter will make up $\frac{1}{3}$ the volume of the solution. The volume of the solution at this point should not greatly exceed 75 ml. It is also better that the amount of ceria present should not exceed about 0.15 g., since the precipitate is bulky, and the washing is rendered more difficult by the very large precipitate. About 0.5 g. of solid potassium bromate is added, and when it has dissolved, an

[13] Cerium is qualitatively detected in a mixture of earths by adding ammonium hydroxide to the acid solution until there is the faintest suggestion of a permanent precipitate. Upon the addition of a few drops of hydrogen peroxide the solution becomes reddish-orange if only a little cerium is present, while in the presence of much cerium a precipitate of the same color separates.

[14] Wyrobouff and Verneuil, Bull. Soc. Chim. [3], **19**, 219, 1898.

[15] Browning and Roberts, Am. J. Sci. [4], **29**, 45, 1910.

[16] E. J. Roberts, Chem. News, **103**, 393, 1911.

[17] James and Pratt, J. Am. Chem. Soc., **33**, 1326, 1911.

[18] Prandtl and Lösch, Z. anorg. allgem. Chem., **127** 209, 1923.

[19] Prandtl and Lösch, *ibid.*, **122**, 159, 1922.

[20] Brinton and James, J. Am. Chem. Soc., **41**, 1080, 1919.

amount of potassium iodate which is not less than 50 times the weight of the estimated cerium dioxide present is added in form of a solution containing 100 g. of potassium iodate and 333 ml. of concentrated nitric acid per liter. The reagent is slowly added with constant stirring. The precipitate of ceric iodate is allowed to settle in the cold until the supernatant liquid is practically clear, and it is then filtered on a paper of close texture, such as Whatman No. 42, or S. and S. blue ribbon. In filtering the precipitate is brought as completely as possible onto the paper with the mother liquor, and the beaker is rinsed just once with a small amount of a solution of 8 g. of potassium iodate and 50 ml. of concentrated nitric acid per liter. After draining, but not standing longer than is necessary, the precipitate is rinsed from the paper back into the beaker with more of the washing solution. Any clots should be broken up with a rod and the mixture well churned. The precipitate is again brought on the filter paper in the same way, and allowed to drain. It is then rinsed back into the beaker with hot water, heated to boiling, with constant stirring, and concentrated nitric acid is dropped in until the precipitate is completely dissolved. Any unnecessary excess of nitric acid is to be avoided. To the solution 0.25 g. of potassium bromate and about the same amount of potassium iodate solution originally used are added. If the use of the iodate solution would unduly increase the volume, the correct amount of the salt can be dissolved by heating in a small volume of 1 : 2 nitric acid and added in that form. The precipitate is allowed to settle as before, and the perfectly cold mixture is filtered through the original paper, given one very small washing with the nitric acid—potassium iodate washing solution, rinsed back into the beaker with, the same solution, well churned, and finally brought onto the paper and washed with 3 small portions of the washing solution. Every trace of ceric iodate need not be removed from the beaker. The paper and precipitate are dropped into the original beaker, any trace of precipitate removed from the funnel with a fragment of "ashless" paper. About 5–8 g. of oxalic acid crystals are now added, and then 50 ml. of water. The covered beaker is heated gently, and the contents are finally boiled until iodine vapors are no longer given off, and all sublimed iodine is vaporized from the cover glass and upper edges of the beaker. After standing several hours the cerous oxalate and filter pulp are filtered, washed with cold water, and ignited to constant weight over the blast. The weight of CeO_2 is obtained by deducting the weight of the two paper ashes.

The sum of the other rare-earths can be determined in the combined filtrates from the ceric iodate by precipitation with sodium hydroxide, solution in hydrochloric acid, precipitation as oxalates and ignition to oxide, finishing in hydrogen if the weight of the sesquioxides is desired.

Volumetric Determination.—Two volumetric methods for the determination of cerium in the presence of other rare-earths give accurate results if attention is paid to certain details. The methods are alike in principle.

1. *The Persulfate Method of von Knorre-Willard and Young.*[21]—The sample, usually mixed oxides obtained from the ignition of oxalates, is moistened with water and then digested with concentrated hydrochloric acid until solution is complete. Ten ml. of concentrated sulfuric acid are added and the mixture is

[21] von Knorre, Z. f. angew. Chem., **10**, 685, 717, 1897; Ber., **33**, 1924, 1900. Willard and Young, J. Am. Chem. Soc., **50**, 1397, 1928.

evaporated to copious fumes to expel all hydrochloric acid.[22] After cooling, the sulfates are dissolved in cold water and diluted to about 200 ml. Five ml. of a solution of 2.5 g. of silver nitrate per liter are added as catalyst, and then 5 g. of solid ammonium persulfate. The solution is boiled 10 minutes, cooled to room temperature and titrated electrometrically with ferrous sulfate solution (about 0.05 normal) which has been standardized against a ceric sulfate solution of known strength.[23]

2. *The Sodium Bismuthate Method of Metzger.*[24]—Fully as accurate, and more convenient for an occasional determination, is the bismuthate method. The sample is brought into solution just as has been described for the persulfate method, except that 20 ml. of concentrated sulfuric acid are to be used instead of 10 ml. The sulfate mass is cooled, about 2 g. of ammonium sulfate crystals are added, and then, carefully, 80 ml. of cold water. About 1 g. of sodium bismuthate is introduced and the solution is heated slowly to the boiling point. After cooling somewhat, 50 ml. of 2% sulfuric acid are added and the solution is filtered from excess bismuth salt by gentle suction through asbestos. While a Gooch crucible will serve, the most convenient filter is a glass funnel with a well-fitting perforated porcelain plate (Witte plate) which has been covered and sealed in place with a reasonably thick felt of asbestos fibre, which has been heated with nitric acid and well washed. After passing the ceric sulfate solution through the filter the latter is washed with 100 to 150 ml. of 2% sulfuric acid. The ceric solution is treated with a measured excess of ferrous ammonium sulfate solution (10 g. of the crystallized salt and 50 ml. of concentrated sulfuric acid per liter) as shown by the disappearance of the yellow ceric color, and the excess of ferrous solution is then titrated back with 0.025 normal potassium permanganate to a pink end-point that will persist for half a minute.

The permanganate is standardized against sodium oxalate in the approved manner. To establish the relationship between the permanganate and the ferrous solution, which should be checked daily, a mixture of 80 ml. of water, 20 ml. of concentrated sulfuric acid, 2 g. of ammonium sulfate and 1 g. of sodium bismuthate are heated to boiling, filtered through the asbestos and washed with 100 ml. of 2% sulfuric acid. To this solution 25 ml. of the ferrous solution are added from a pipette and tirated with the permanganate. From this blank the volume of permanganate solution equivalent to the volume of ferrous ammonium sulfate added to the ceric solution is calculated. The difference between this calculated volume and that used in the back titration of the excess of ferrous solution in the analysis of the cerium sample gives the volume of permanganate equivalent to the cerium in the sample. Since the change undergone by the cerium is from trivalency to quadrivalency, 1 ml. of normal $KMnO_4$ is equivalent to 0.14013 g. of Ce, or to 0.17213 g. of CeO_2.

[22] While the sample may be dissolved directly in sulfuric acid by long digestion, and must be so dissolved if the ceria in the sample amounts to more than about 50%,—since such mixtures are very difficultly soluble in hydrochloric acid,—yet for most samples the method here given is more rapid, has the advantage of allowing one to see when solution is complete (which cannot readily be done in the syrup of sulfates in sulfuric acid), and the resulting sulfates seem more readily soluble in water than when the sample has been treated with sulfuric acid from the start.

[23] Willard and Young, J. Am. Chem. Soc., 51, 149, 1929.

[24] J. Am. Chem. Soc., 31, 523, 1909. Cf. Furman, ibid., 50, 755 (1928).

Different lots of sodium bismuthate vary considerably in purity. If a reagent of high purity is at hand the establishment of the ratio between ferrous and permanganate solutions may be carried out by simply titrating in dilute sulfuric acid solution. Someya [25] states, moreover, that filtration of the excess bismuth salt,—presumably all in the quinquivalent state after the boiling,—is unnecessary.

With the best samples of sodium bismuthate which the writer has been able to purchase, the omission of the filtration has made a difference of the order of a few tenths of one per cent in the reported figures for cerium. This may not be of consequence for many routine analyses, but for unknown lots of bismuthate the procedure detailed above is safer, and it really takes very little longer, once the asbestos filter has been prepared, since it may be used for a great number of determinations.

DETERMINATION OF EUROPIUM

Trivalent salts of europium can be reduced to the divalent stage in a number of ways.[26] On the basis of reduction by zinc, McCoy has developed an iodometric method for the determination of europium in the presence of other rare-earths. The mixture of oxides, free from phosphate, sulfate and iron, is dissolved in hydrochloric acid, and diluted to give an acidity of 0.1–0.2 N. The solution is poured through a Jones reductor (charged with 20–30 mesh amalgamated zinc in the conventional way), the tip of which dips into an excess of approximately 0.04 N iodine solution. The excess of iodine is titrated with standard sodium thiosulfate solution. The transfer of one electron per ion is involved, so the milliequivalent of europium (Eu) is 0.152, while that of the sesquioxide (Eu_2O_3) is 0.352.

[25] Z. anorg. allgem. Chem., **168**, 56, 1927.

[26] L. F. Yntema, J. Am. Chem. Soc., **52**, 2782, 1930; P. W. Selwood, ibid., **57**, 1145, 1935; H. N. McCoy, ibid., **57**, 1756, 1935; **58**, 1577, 2279, 1936.

JUDGMENT OF THE COMPOSITIONS OF THE GROUPS

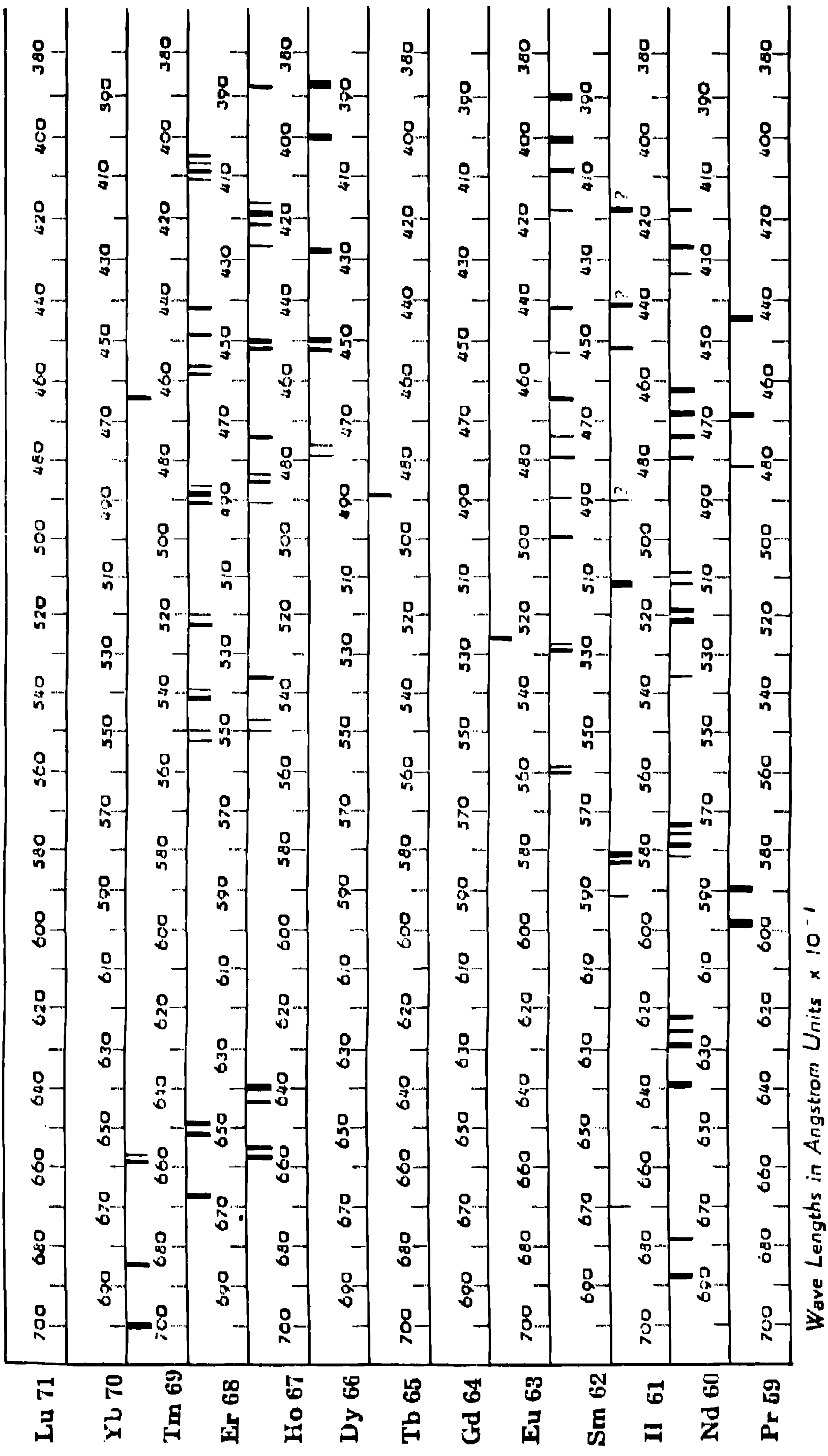
In the preceding sections methods have been given whereby one may tell accurately the percentage of the total rare-earths in a sample, and the proportion of cerium in that total. The sum of the remaining earths may further be approximately divided into the " cerium group " and the " yttrium group " by the double sulfate precipitation. The further problem of telling just what elements are in the two groups is one that is usually considered unnecessary by most chemists who are not pursuing research in this particular field. By very long processes of fractional crystallization the most complex mixture of rare-earths can be separated into a number of portions in which the qualitative composition can be determined, and the relative amount of each element judged approximately, but such a procedure would require months of work and a very large amount of material. The description of such a process is without the scope of this chapter, and it must suffice to cite the reference to the most reliable and comprehensive scheme [27] that has yet been worked out. Qualitatively, however, valuable information can be obtained by methods that will now be described.

Absorption Spectra.—Praseodymium, neodymium, samarium, dysprosium, holmium, erbium, and thullium solutions give absorption spectra in the visible region which can be readily seen with any ordinary glass prism spectroscope of reasonably good grade. A small direct vision spectroscope will serve an experienced observer.

The material to be examined is brought into solution in nitric acid, and this solution in a glass vessel (an ordinary beaker serves for qualitative observation) is placed closely up in front of the slit of the spectroscope, and a bright electric light bulb is set directly behind the solution. The absorption bands can then be seen as dark vertical lines of varying breadth against the bright background of the colored continuous spectrum given by the light. The sun, a bright cloudy sky, or a sheet of white paper in sunlight may also serve as sources of illumination. The breadth and intensity of the bands naturally increase with increasing concentration of the solution and with increasing thickness of the layer of the solution. Moreover, the nature of the solvent and the degree of acidity affect somewhat the intensity and the exact position of the bands, but for rough qualitative examination these variations have no great significance. It is customary to make the examination in a nitrate solution that is only slightly acid. If the solution is too rich in neodymium the whole field may be obscured to the point where observation of the bands of other earths is practically impossible, since neodymium has bands of great width and intensity. In such cases the solution must be diluted, but it will be understood that if very much neodymium and comparatively little of the other colored earths are in the solution the dilution might have to be carried to a point where the minor constituents were no longer detectable.

If a spectroscope is available which gives readings in direct wave-lengths the identification of the lines is not difficult, and the table by Harris and Hopkins, J. Am. Chem. Soc., **48**, 1593, 1926, showing all the most prominent absorption bands and their relations to each other is shown below.

[27] C. James, J. Am. Chem. Soc., **34**, 757, 1912.


Lu 71
Yb 70
Tm 69
Er 68
Ho 67
Dy 66
Tb 65
Gd 64
Eu 63
Sm 62
Il 61
Nd 60
Pr 59
Wave Lengths in Angstrom Units x 10⁻¹

Many of the lines shown there in groups will, when observed through a small spectroscope, appear as single lines.

If the spectroscope has only an arbitrary scale the latter can be made to serve quite well by determining upon the scale the positions of well known flame spectrum lines. Thus the three main absorption bands of praseodymium [28] will be a heavy line (444 $\mu\mu$) in the blue falling on the violet side of the shortest wave-length cesium twin, a fainter line (468 $\mu\mu$) falling about equally far on the red side of the other cesium blue line, and a third line (482 $\mu\mu$), yet fainter, found still farther to the red side. The relative distance from the second line may be roughly judged by the approximate wave-lengths here given. In the case of neodymium the broadest line (572–578 $\mu\mu$) will be found in the yellow just a shade to the violet side of the well known sodium line. The two next most important lines of neodymium (521 $\mu\mu$ and 510 $\mu\mu$) are found in the green in the neighborhood of the most intense (α) line of barium. Samarium is readily recognized by very wide, diffuse lines which cause a blur in the blue not far from the violet side of the visible region, around the Frauenhofer F line of the sun spectrum. The single line of europium (525 $\mu\mu$), in examination with a small spectroscope, is almost coincidental with the 521 line of neodymium, but it can be distinguished as falling a little farther to the red side. This line and the terbium line (488 $\mu\mu$) can never be seen in any naturally occurring mixture of earths owing to the scarcity of these earths and the faintness of their lines. (After a short period of fractional crystallization of the double magnesium nitrates of the monazite earths the europium line can be seen in the most soluble fractions.) The absorption lines of dysprosium are easily confused with those of samarium, though with good lenses and prisms, and intense illumination, the line at about 428 $\mu\mu$ at the edge of the blue, not far from the Frauenhofer G line, can be seen, and it is quite characteristic in the absence of too much neodymium. (Neodymium can always be removed by potassium sulfate.) Holmium is rich in lines, several in the green and many in the blue. A line in the red (657 $\mu\mu$), coming between the red lithium and the orange calcium lines, can be confused only with a line of thulium at about the same place, but the stronger lines of thulium at 684 $\mu\mu$, to the red side of the lithium line, and at 465 $\mu\mu$, slightly to the red side of the blue strontium line, will help to decide between holmium and thulium. Erbium is easily detected, and it is very prevalent in almost all yttrium group mixtures occurring in nature, by its characteristic lines at about 667 $\mu\mu$, just to the violet side of the red lithium line, and at 648 $\mu\mu$, coming in the red between two holmium lines. Erbium is also rich in lines in the blue, and some in the green, but the ones cited will serve for identification.

If only a direct vision spectroscope, with no scale, is at hand, the wave-lengths can be judged approximately for the identification of praseodymium, neodymium, samarium and erbium by the position of the Frauenhofer lines, observed by looking through the instrument at the sun or bright sky.

Arc and Spark Spectra.—Only certain of the rare-earths give absorption spectra, but all of them give arc spectra. The most characteristic lines are apt to lie in the ultra-violet region, so one must work with a quartz spectrograph and

[28] The data given in this section are intended entirely for practical application, and the wave-lengths are only approximate. Only the most important lines of the rare-earths that are visible in moderate concentrations are mentioned.

the lines must be photographed. A small amount of the solid, or a drop or two of the concentrated solution, is brought into the cavity of the lower pole (purified carbon or copper) and a direct current arc of about 6 amperes at 110 volts is passed. The light is focussed upon the slit of the spectrograph by means of a quartz condensing lens. To complete the observation it is necessary to throw upon the photographic plate an image of the iron arc directly above, and of the blank electrodes directly below the image of the sample. The wave-lengths of the lines in the iron arc are well known, and they serve as points of reference for the identification of the lines of the various earths. The arc spectra serve especially to test the purity of given samples.[29] The wave-lengths of the various elements are given in several larger works, and these must be consulted for data and details of manipulation.[30] Once the apparatus is assembled and adjusted the arc spectrum method is very rapid and convenient. The only drawback is that it entails a slight loss of (frequently very valuable) material.

The method of photographing spark spectra is not very different from that for arc spectra. The light is produced, however, by passing a condensed spark between platinum electrodes, the negative of which is moistened with the solution under investigation. The arc and spark spectra for a given element are not identical, but each is characteristic. Details of practice for spark spectra will be found in the works referred to for arc spectra.

Determination of Average Atomic Weight.—Since yttrium has an atomic weight that is very low compared with the others, a determination of the average atomic weight of the elements in a sample of the yttrium earths will give considerable information as to the presence and probable amount of the other, and rarer, members of the group. The method presupposes the absence of cerium and praseodymium; and terbium, if in appreciable amount, must have been brought to the sesquioxide by ignition in hydrogen. A weighed amount of the oxides (0.1 to 0.15 g.) is dissolved by heating in exactly 50 ml. of accurately standardized sulfuric acid (about 0.1 normal). About 8 ml. of potassium oxalate solution (approximately 0.2 normal) is added, and the mixture is boiled. After cooling, phenolphthalein is added, and the excess sulfuric acid is titrated back with 0.1 normal sodium hydroxide. The precipitated rare-earth oxalates do not interfere. From the weight of the oxide and that of the sulfuric acid which reacted with it the average atomic weight of the elements concerned can be calculated by the methods of elementary chemistry.

In the preceding paragraphs of this section methods have been given for telling something about the qualitative composition of a given sample, but so far we have only succeeded in dividing our group into three minor groups: (*a*) pure ceria, (*b*) the remainder of the ceria group, and (*c*) the yttria group. Without attempting long processes of fractionation can we accomplish more in the separation of items (*b*) and (*c*)? Unfortunately it is not practicable. The

[29] P. W. Selwood, Ind. Eng. Chem., Anal. Ed., 2, 93, 1930.

[30] H. Kayser, Handbuch der Spectroscopie, 7 vols., Leipzig (1900–1924), and the same author's Tabelle der Hauptlinien der Linienspektren aller Elemente (1926); Bardet, Atlas of Arc Spectra, Paris; International Critical Tables. Anyone planning work along this line should write to Adam Hilger, Ltd., 24 Rochester Place, London, N.W. 1, England, for description of apparatus, and books on wave-lengths and technique; and to the U. S. Bureau of Standards, Washington, D. C., for a list of their pamphlets dealing with the subject.

best that can be done with the yttrium elements in a reasonable amount of time is to determine the average atomic weight, and thus decide whether the mixture is made up preponderantly of yttrium or of the rarer elements, and then to identify as many of the elements as possible spectroscopically. For the cerium group, after having removed cerium, various modifications of the method of heating the nitrates have been proposed, whereby a separation could be effected in a few operations. These aim at reaching a temperature at which the less basic members are decomposed more or less into difficultly soluble basic nitrates, while the more strongly basic lanthanum remains in the nitrate form and is completely soluble in water. However useful this may be as a gradual fractionation method, it seems that to attain anything approaching a sharp separation the conditions must be varied for each individual mixture, and the adjustment needed is so delicate that most chemists who have tried the separation have not been really successful. The spectroscope and spectrograph still give the most reliable information.

Knowledge of the colors of the solutions of the earths is often helpful. Those of lanthanum, cerous cerium, gadolinium, terbium, yttrium, ytterbium and lutecium are colorless. Europium solutions are very light pink, erbium deeper pink and neodymium reddish violet. Samarium and holmium give yellow solutions, while those of ceric salts are deep reddish orange. The solutions of praseodymium, dysprosium and thulium are green. The color of illinium solutions is not known.

Cerium, lanthanum, neodymium, yttrium, praseodymium, samarium and erbium may be met in large to fair amounts, decreasing perhaps roughly in the order given. The other rare-earths are usually present in such small quantities that until they have been specially concentrated in the laboratory their amounts are unimportant.

CHLORINE[1]

Cl_2, *at.wt.* 35.457; *D.* (*air*), 2.491; *m.p.* −101.6°C.; *b.p.* −34.6° C.; *oxides*, Cl_2O, ClO_2, Cl_2O_7

Chlorine occurs combined in nature generally with sodium, potassium and magnesium. It is a component of rock forming minerals such as sodalite. It occurs in the minerals rock salt, halite, NaCl; sylvine, KCl; carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$; and combined in minerals of copper, lead, silver, etc. It occurs more commonly in rocks high in sodium and low in silica, but is also found in quartz bearing ores. It occurs in sea water, mineral springs and ground waters. It is widely distributed in nature.

DETECTION

Free Chlorine.—The yellow gas is recognized by its characteristic odor. It liberates iodine from iodides; it bleaches litmus, indigo, and many organic coloring substances.

Chlorides. Silver Nitrate Test.—In absence of bromides and iodides, which also form insoluble silver salts, silver nitrate precipitates from solutions containing chlorides white, curdy, silver chloride, AgCl (opalescent with traces), soluble in NH_4OH (AgBr slowly soluble, AgI difficultly soluble), also soluble in concentrated ammonium carbonate (AgBr is very slightly soluble; AgI is insoluble). Silver chloride turns dark upon exposure to light.

Free Hydrochloric Acid. Manganese Dioxide, Potassium Permanganate, and certain oxidizing agents liberate free chlorine gas when added to solutions containing free hydrochloric acid. The gas passed into potassium iodide liberates free iodine, which produces a blue solution with starch.

Concentrated Sulfuric Acid added to chlorides and heated liberates HCl gas, which produces a white fume in presence of ammonium hydroxide.

Detection in Presence of Cyanate, Cyanide, Thiocyanate.—An excess of silver nitrate is added to the solution, the precipitate filtered off and boiled with concentrated nitric acid to oxidize the cyanogen compounds and the white

[1] The element, first obtained by Scheele by the action of pyrolusite, MnO_2, on hydrochloric acid ("marine acid") in 1774, finds extended uses, bleaching, germicide, extraction of gold from its ores, chemical industries, etc. Among the compounds—table salt, NaCl, chlorides, chlorates, perchlorates, hypochlorites are well known.

precipitate, silver chloride, subjected to the tests under chlorides to confirm the compound.

If Chlorates are Present.—The halogens are precipitated with silver nitrate, the precipitate dissolved with zinc and sulfuric acid and the solution treated as directed in the preceding paragraph.

Test for Hypochlorite.—Potassium hypochlorite, $KClO$, shaken with mercury forms the yellowish-red compound Hg_2OCl_2,[2] which does not form with the other potassium salts of chlorine, i.e., KCl, $KClO_2$, $KClO_3$, $KClO_4$.

Hypochlorites decolorize indigo, but do not decolorize potassium permanganate solutions. If arsenious acid is present, indigo is not decolorized until all of the arsenious acid has been oxidized to the arsenic form.

Tests for Chlorite.—Potassium permanganate solution is decolorized by chlorites. (The solution should be dilute.)

A solution of indigo is decolorized, even in presence of arsenious acid (distinction from hypochlorites).

Detection of Chlorate.—The dry salt heated with concentrated sulfuric acid detonates and evolves yellow fumes.

Chlorates liberate chlorine from hydrochloric acid.

Perchlorate.—The solution is boiled with hydrochloric acid to decompose hypochlorites, chlorites and chlorates. Chlorides are removed by precipitation with silver nitrate, the filtrate evaporated to dryness, the residue fused with sodium carbonate to decompose the perchlorate to form the chloride, which may now be tested as usual.

Detection in Presence of Bromide and Iodide.—About 10 ml. of the solution is neutralized in a casserole with acetic acid, adding about 1 to 2 ml. in excess, and then diluting to about 6 volumes with water. About half a gram of potassium persulfate, $K_2S_2O_8$, is added and the solution heated. Iodine is liberated and may be detected by shaking the solution with carbon disulfide, which is colored violet by this element. Iodine is expelled by boiling, the potassium persulfate being repeatedly added until the solution is colorless. Bromine is liberated by adding 2 or 3 ml. of dilute sulfuric acid and additional persulfate. A yellowish-red color is produced by this element. Carbon disulfide absorbs bromine, becoming colored yellowish red. Bromine is expelled with additional persulfate and by boiling. The volume of the solution should be kept to about 60 ml., distilled water being added to replace that which is expelled by boiling. When bromine is driven out of the solution, the silver nitrate test for chlorides is made. A white, curdy precipitate, soluble in ammonium hydroxide and reprecipitated upon acidifying with nitric acid, is produced, if chlorides are present.

[2] Prescott and Johnson, Qual. Chem. Anal. D. Van Nostrand Co.

ESTIMATION

The determination of chlorine is required in a large number of substances. It occurs combined as a chloride mainly with sodium, potassium and magnesium. Rock salt, NaCl, sylvine, KCl, carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$, matlockite, $PbCl_2 \cdot PbO$, horn silver, AgCl, atacamite, $CuCl_2 \cdot 3Cu(OH)_2$, are forms in which it is found in nature. Chlorine is determined in the evaluation of bleaching powder. It is estimated in the analysis of water.

Many of the chlorides are easily soluble in water. Chlorides of insoluble compounds such as lead and silver may be readily decomposed by fusion with sodium or potassium carbonate; the mercurous chloride by digestion with sodium or potassium hydroxide.

PREPARATION AND SOLUTION OF THE SAMPLE

In dissolving the sample the following facts should be borne in mind: Although chlorides are nearly all soluble in water, silver chloride is practically insoluble (100 ml. dissolve 0.000152 gram at 20° C.); mercurous chloride is nearly as insoluble as silver chloride (0.00031 gram); lead chloride requires heat to bring it into solution (in cold water only 0.673 gram soluble per 100 ml. of water). Chlorides of antimony, tin, and bismuth require free acid to keep them in solution. Hydrochloric acid increases the solubility of silver, mercury, lead, antimony, bismuth, copper (Cu′), gold and platinum, but decreases the solubility of cadmium, copper (Cu″), nickel, cobalt, manganese, barium, calcium, strontium, magnesium, thorium, sodium, potassium and ammonium chlorides.

Chlorine gas is most readily dissolved in water at 10° C. (1 vol. H_2O dissolves 3.095 vols. Cl). Boiling completely removes chlorine from water.

Hypochlorites, chlorites, chlorates, and perchlorates are soluble in water.

The chlorine may be present either combined or free. In the combined state it may be present as free hydrochloric acid or as a water-soluble or insoluble salt.

Water-soluble Chlorides.—Chlorides of the alkali or alkaline earth groups may be treated directly with silver nitrate upon making slightly acid with nitric acid, the chlorine being determined either gravimetrically or volumetrically according to one of the procedures given later. It is convenient to work with samples containing 0.01 gram to 1 gram of Cl. The sample is dissolved in about 150 ml. of water, made acid with nitric acid with about 5 to 10 ml. in excess of the point of neutralization, should the sample be alkaline. Then the chlorine combined as chloride is determined as directed later.

If the water solution contains a chloride of a heavy metal which forms basic salts (e.g., stannic, ferric, etc., solutions), or which may tend to reduce the silver solution, it is necessary to remove these by precipitation with ammonium hydroxide, or by sodium hydroxide, or potassium carbonate solution. The salt is dissolved in water and acidified with HNO_3, adding about 10 ml. in excess, for about 150 ml. of solution. (This excess HNO_3 should be sufficient to oxidize substances which would tend to reduce the silver reagent; e.g., $FeSO_4$, etc.) Ammonia solution (free from chloride) is added in sufficient quantity

to precipitate the heavy metals iron, manganese, aluminum, etc. The mixture is filtered and the residue washed several times with distilled water. Chlorine is determined in the filtrate by acidifying with HNO_3 as directed above.

Water-insoluble Chlorides.—The chloride may frequently be decomposed by boiling with sodium carbonate solution. Many of the minerals, however, require fusion with sodium carbonate to prepare them for solution; e.g., apatite, sodalite, etc. Silver chloride may also be decomposed by fusion.

Silver Chloride.—The sample is mixed with about three times its weight of Na_2CO_3 and fused in a porcelain crucible until the mass has sintered together. The soluble chloride, NaCl, is leached out with water, leaving the water-insoluble carbonate of silver, which may be filtered off. The filtrate is acidified with HNO_3 and chlorine determined as usual.

Chlorine in Rocks.—The finely ground material is fused with about five times its weight of potassium carbonate. The melt is extracted with hot water, cooled and the solution acidified with nitric acid (methyl orange indicator), and the solution allowed to stand several hours (preferably over night). If silicic acid precipitates, the solution is treated with ammonia and boiled, filtered and the filter washed with hot water. The cooled filtrate is acidified with nitric acid and chlorine determined as usual. If silicic acid does not separate, the addition of ammonia may be omitted and chlorine determined in the solution.

Free Chlorine.—Free chlorine may be determined volumetrically according to the procedure given under this section. If it is desired to determine this gravimetrically, a definite amount of the chlorine water is transferred by means of a pipette to a flask containing ammonia solution and the mixture heated to boiling. The cooled solution is acidified with nitric acid and the chloride precipitated with silver nitrate according to the standard procedure given on page 269.

NOTE.—Free chlorine cannot be precipitated directly, as the following reaction takes place: $6Cl+6AgNO_3+3H_2O=5AgCl+AgClO_3+6HNO_3$.

Reaction of chlorine with ammonia: $2Cl+2NH_4OH=NH_4Cl+NH_4OCl+H_2O$. When the solution is boiled, NH_4OCl breaks down, e.g., $3NH_4OCl+2NH_3=3NH_4Cl+N_2+3H_2O$.

Chlorine in Ores and Cinders.—One hundred grams of the finely ground ore or cinder are placed in a 500-ml. flask, containing 300 ml. of conc. sulfuric acid (Cl-free). The flask is shaken to mix the sample with the acid and then connected with an absorption apparatus, containing distilled water or dilute caustic solution. The sample is gradually heated, the distillation flask resting upon a sand bath. After two hours, which is sufficient to expel all the chlorine as hydrochloric acid, the contents of the absorption tubes are filtered, if free sulfur is present (sulfide ores), nitric acid added and the filtrate brought to boiling to oxidize any SO_2 that may be present. Chlorine is precipitated according to the standard procedure on page 269.

During the run the distilling flask should be shaken occasionally to prevent caking. Suction applied at the absorption end of the apparatus and a current of air swept through the system aids in carrying over the HCl into the water or NaOH.

Determination of Halogens in Organic Compounds. Method of Carius [3]

Organic compounds may be decomposed by heating with conc. nitric acid at high temperatures under pressure. If this heating is conducted in the presence of silver nitrate, the halogen hydride, formed by the action of nitric acid on the organic compound, is converted to the silver halide. This is weighed, or the excess $AgNO_3$ titrated (p. 271). Arsenic, phosphorus, and sulfur are oxidized to arsenic, phosphoric, and sulfuric acids, the metals present being converted to nitrates.

Procedure.—About 0.5 to 1 gram of powdered silver nitrate is introduced, by means of a glazed paper funnel, into a heavy-walled, bomb-glass tube, which is sealed at one end and is 50 cm. long, 2 cm. in diameter and about 2 mm. thickness of wall. About 3 ml. of fuming nitric acid (96%), free from chlorine, are introduced by means of a long-stemmed funnel, to avoid wetting the upper portion of the tubing. About 0.1 gram of the organic substance, contained in a small bore, thin wall, glass tube closed at one end (4–5 cm. long), is introduced into the bomb tube, inclined to one side. The small tube should float in the nitric acid, as it is important that the material should not come in contact with nitric acid until the bomb has been sealed, as loss of halogen is apt to occur with open tubes. The upper end of the bomb is softened in the blast-lamp flame, drawn out to a thick-walled capillary tube and fused.

When cold, the bomb is wrapped in asbestos paper, shoved into an iron tube of a bomb furnace and the heat turned on. The heating is so regulated that the temperature is raised to 200° C. in three hours. If a higher temperature is necessary, the heating should be such as to cause a rise of 50° C. in three hours. Substances of the aromatic series require eight to ten hours heating at 250 to 300° C., while aliphatic substances may be decomposed at 200° C. in about four hours.[4] Occasionally it is necessary to relieve the pressure in a tube after heating to 200° C., before taking to a higher temperature, by softening the tip of the cooled bomb in a flame, allowing the accumulated gas to blow out, resealing and again heating to the desired temperature. Evidence of crystals or drops of oil in the glass tube indicates incomplete decomposition. When the bomb is cooled, it is removed by taking out the iron sheath from the furnace and inclining it so that the glass capillary tip slides partly out of the tube. (The eyes should be protected by goggles.) The point of the capillary is held in the flame until the tip softens and the gas pressure is released by blowing through a passage in the softened glass. When the gas has escaped, a scratch with a file is made below the capillary and the tip broken off by touching the scratch with a hot glass rod. The contents of the bomb are poured out into a beaker, the tube washed out with water and the combined solution made to about 300 ml. This is heated to boiling and then allowed to cool. The halide precipitate is filtered through a Gooch crucible, then dried and weighed, or by titrating the excess $AgNO_3$ by Volhard's method, the halide may be estimated.

NOTE.—The amount of HNO_3 should not exceed 4 grams per 50-ml. tube, as larger amounts may cause an explosion—Fresenius, Quant. Chem. Anal., **2**, 118, 1915 (J. Wiley & Sons).

[3] Ann. d. Chem. u. Pharm., **136**, 129, 1865.

[4] O. Tomicek, Chem. Ztg., **49**, 281, 1925. P. C. R. Kingscott and R. S. G. Knight, Methods of Quant. Org. Anal., Longmans, Green & Co. (1914). Clowes and Coleman, Quant. Chem. Anal., P. Blakiston's Son & Co., 1900.

If pieces of glass should be present, the precipitates, AgCl or AgBr, are dissolved in ammonium hydroxide, filtered and reprecipitated by acidifying with nitric acid. AgI may be dissolved by means of dilute sulfuric acid and zinc. The excess zinc is removed, the glass washed free of iodine, dried and weighed and its weight subtracted from the original impure AgI, giving the weight of the pure silver iodide.

SODIUM AND ALCOHOL METHOD (STEPANOV) [5]

A solution of the organic substance in 98% alcohol is treated with a large excess of sodium added in small portions over a period of 30 minutes.

Procedure.—Place the substance in a small Erlenmeyer flask, add 20–40 ml. of 98% alcohol, connect the flask to a vertical condenser and warm on a water bath. Add small pieces of sodium (25-fold excess) through the condenser, after the sodium has dissolved, add 20–40 ml. of water and distill off the alcohol. Finish the determination by any standard volumetric or gravimetric procedure. If a represents the weight of the sample in gram, then the relative amounts of alcohol and sodium should be as follows:

	Ml. of 98% Alcohol	Sodium to be used, gram
If chloride is present	$156 \times a$	$19.5 \times a$
If bromide is present	$68 \times a$	$8.5 \times a$
If iodide is present	$44 \times a$	$5.5 \times a$

SODIUM AND LIQUID AMMONIA METHOD (DAINS) [6]

A 0.1–0.2 g. sample, accurately weighed, of the substance is dissolved in 30–50 ml. of liquid ammonia in a small open Dewar vessel. Small clean pieces of sodium are added until the blue color persists for ½ hour. The ammonia is then allowed to evaporate, the process being hastened with an air draft. A little alcohol is added to react with any sodium that remains, then water is added and the determination is completed by any convenient method.

In a few cases cyanide is formed or remains after the sodium treatment, namely in the cases of chloroform, bromoform, carbon tetrachloride, chloral hydrate, bromal hydrate, ethylidene chloride, tetrachloroethylene, acetylene tetrachloride, methyl cyanide, benzyl cyanide and ethyl cyanoacetate. If cyanide is present, or in any doubtful case, transfer the solution to a 250 ml. beaker, dilute to 200 ml., and neutralize (Hood) with acetic acid to phenol phthalein, and add 1 ml. of 6 N acetic acid in excess. Boil the solution for 1 hour, keeping the volume between 150 and 200 ml. by adding distilled water as may be necessary. After the HCN has been expelled, complete the determination of the halide by a standard method.

LIME METHOD FOR DETERMINATION OF HALOGENS IN ORGANIC MATTER

A layer of lime (free from chloride), about 6 cm. long, is introduced into a difficultly fusible glass tube, closed at one end (35 cm. long and with 1 cm.

[5] Stepanov, Ber., 31, 4056 (1906); Tseng, Hu and Chiang, J. Chinese Chem. Soc., 3, 223 (1935).

[6] Dains, J. Am. Chem. Soc., 40, 936 (1918); Dains and Brewster, ibid., 42, 1574 (1920); Clifford, ibid., 41, 1051 (1919).

bore), followed by 0.5 gram of the substance, and 6 cm. more of the lime. The substance is thoroughly mixed by means of a copper wire with a spiral end. The tube is nearly filled with lime and, in a horizontal position, gently tapped to cause the lime to settle and form a channel above the layer. The tube is placed in a small carbon combustion furnace. The heat is turned on, so that the front end of the tube is heated to dull redness and then the end containing the substance. When the organic matter has been decomposed, the tube is cooled and the contents transferred to a beaker and the lime dissolved in dilute nitric acid (Cl-free). The carbon is filtered off and the halogen determined as usual in the filtrate.

Should a sulfate be present in the mixture, organic matter will reduce it to a sulfide, so that Ag_2S will be precipitated along with the halides. To prevent this, hydrogen peroxide is added to the solution, which should be slightly alkaline. The mixture is boiled to remove the excess of H_2O_2 and is then acidified with nitric acid, the solution filtered and the halide determined in the filtrate.

With substances rich in nitrogen, some soluble cyanide is apt to form. The silver precipitate containing the halides and the cyanide is heated to fusion. The residue is now treated with zinc and sulfuric acid, the metallic silver and the paracyanogen filtered off and the halides determined in the filtrate.

Sodium Peroxide Method

Organic compounds may be decomposed by sodium peroxide in an open crucible without recourse to a sealed tube, as is required by the Carius method. The following is the procedure outlined by Pringsheim.[7]

About 0.2 gram of substance in a small steel crucible is treated with a calculated quantity of sodium peroxide.[8] The crucible should be only two-thirds of its height full; this is put in a large porcelain crucible, in which a little cold water is carefully placed, so that the steel crucible stands out 1 to 2 cm. This latter crucible is covered with its own cover, in which is a hole through which an iron wire heated to redness can be introduced with the object of starting the combustion. As soon as the combustion is completed the whole is plunged into the water in the larger crucible. The porcelain crucible is covered with a watch-glass and heated gently until the whole mass is dissolved. This point is recognized when no more bubbles are given off and when there are no more particles of carbon which have escaped combustion. The steel crucible is then removed and washed carefully; the solution is filtered and treated with an excess of sulfurous acid (to neutralize the alkaline liquid, and to reduce the oxidized products: bromic, iodic acids, etc.). The solution is acidulated with

[7] C. N., 91, 2372, 215, 1905.

[8] Charge of sodium peroxide is judged as follows:

Per cent C and O in material	Amount of sugar to add	Amount of Na_2O_2 required
Over 75	0	18 times wt. of sub.
30 to 75	0	16 times wt. of sub.
25 to 50	½ the wt. of sub.	16 times wt. of sub.
Below 25	An equal weight	16 times wt. of sub.

nitric acid, then made to a volume of about 500 ml., and the halogens precipitated with silver nitrate and the precipitate washed, dried and weighed as usual.

Chlorine and Chlorides in Gas.—The gas is bubbled through dilute sodium hydroxide contained in one or more cylinders, gas wash bottle type, measuring the gas by means of a dry meter, placed after the cylinders. The meters are protected from moist gas by passing this through sulfuric acid and an asbestos filter, loosely packed. Aliquot portions of the sodium hydroxide are now examined for chlorine by acidifying with nitric acid and adding silver nitrate. If only traces are present the turbidity of the solution is compared with standards made up with known amounts of sodium chloride dissolved in water. The comparisons may be made conveniently in Nessler tubes. To different quantities of the standard made up to a convenient volume, silver nitrate reagent is added and the solution diluted to 50 or 100 ml. The unknown, placed in a Nessler tube, is treated with nitric acid and silver nitrate and matched with the standards, after dilution to the same volume adopted for the standards.

SEPARATIONS

The following separations may be necessary in presence of substances interfering with the chlorine determination. The hydrolysis of antimony and bismuth in solutions not sufficiently acid makes the removal of these elements advisable. The removal of cyanide and the halogens, bromine and iodine, on account of their co-precipitation with chlorine necessitates a preliminary procedure for each as outlined below. These steps are not required in absence of the interfering substances.

Removal of the Heavy Metals from the Halogens.—The solution is boiled with sodium carbonate. The heavy metals precipitate as carbonates while the halogens remain in solution as sodium salts.

Separation of the Halogens from Silver Cyanide and Silver Ion.—The solution is treated with an excess of zinc and sulfuric acid. The metallic silver and the paracyanogen are filtered off and the halogens determined in the filtrate.

Separation of the Halogens. Separation of Iodine from Chlorine.—Iodine may be expelled from the solution by addition of sodium nitrite and sulfuric acid and boiling. The solution diluted to about 700 ml. with water and containing not over 0.25 g. of each halide is treated with about 3 grams of sodium nitrite, 3 ml. of dilute H_2SO_4 (1 : 1) and boiled, the solution being kept to a volume of over 500 ml. The iodine will be completely expelled in about 45 minutes. Chlorine and bromine will remain in the flask. If the determination of iodine is desired its vapor is caught in a 5% solution of NaOH containing 3% of hydrogen peroxide.

Separation of Bromine from Chlorine.—If bromine is present the solution from which the iodine has been expelled as outlined above is neutralized with NaOH and the solution evaporated to about 50 ml. Dilute acetic acid is added to the cooled solution with about 65 ml. excess (glacial acetic 1 water 2). About 1½ g. of $KMnO_4$ crystals are added and bromine expelled by steam distillation. If the determination of bromine is desired it is absorbed in NaOH.

L. W. Andrews (J. Am. Chem. Soc., 29, 275, 1907) recommends oxidation with potassium biiodate, $KH(IO_3)_2$, in dilute nitric acid (0.2 N iodate and 2 N HNO_3). The original article should be consulted.

Considerable work on separation of the halogens was done by F. A. Gooch, "Methods in Chemical Analysis."

GRAVIMETRIC

SILVER CHLORIDE METHOD

The procedure is based on the insolubility of silver chloride in dilute nitric acid solution, the following reaction taking place, M representing a monatomic element:

$$M.Cl + AgNO_3 = M.NO_3 + AgCl.$$

From the equation it is evident that 35.46 grams of chlorine require 169.9 grams of silver nitrate. In practice it is best to add about 20% excess of the silver salt.

Equivalents: 1 gram Cl, 4.79 grams $AgNO_3$, 3.043 grams Ag.

Reagents. ***Silver Nitrate Solution.***—Make up a solution containing 4.8 grams $AgNO_3$ per 100 ml. of distilled water, or dissolve 3.05 grams of silver foil in 10 ml. of dilute nitric acid (1 : 1.6) and make up to 100 ml. One ml. of this reagent will precipitate 0.01 gram of chlorine, or 0.0404+ gram AgCl.

Dilute Nitric Acid.—One vol. HNO_3 to 1.6 vols. H_2O (dist.).

Procedure. Soluble Chlorides. Preparation of the Solution.

1. Weigh 0.4 to 0.5 gram of the salt on a watch glass or in a weighing bottle and transfer to a beaker or an Erlenmeyer flask.

2. Dissolve in 100 ml. of water and add 2 ml. of dilute nitric acid.

3. *Precipitation.*—Calculate roughly the ml. of the silver nitrate reagent that are required to precipitate the chlorine in the sample. If it is an unknown, consider the chlorine in the material to be about 50%. Run the determination in duplicate. The first will be a guide to the amount of silver nitrate solution required.

4. Add the silver nitrate from a burette, drop by drop, to approximately the quantity calculated to be necessary, stirring the solution during the addition. Allow the precipitate to settle and add a few more drops of the reagent, and continue the addition as long as a precipitate forms with the reagent. Now add about 20% in excess.

5. Heat to boiling, covering the beaker with a watch glass.

6. If the solution is still cloudy, stir vigorously. If the solution is in an Erlenmeyer flask, the mixture may be shaken. This will cause the finely divided silver salt to coagulate so that the solution will settle out clear. Avoid

exposing the precipitate to strong light, as this will cause the exposed surface to decompose into the subchloride Ag_2Cl and liberate chlorine.

7. *Filtration.*—Two processes are commonly practiced.

Filter Paper Method.—Decant the clear solution into a filter. Test the filtrate to be sure all chlorine has been precipitated by adding a drop or so of silver nitrate solution. Wash the precipitate in the beaker twice by decantation and then transfer to the filter and wash until free of chlorides. The wash water should contain 1 ml. of nitric acid per 100 ml. of distilled water.

8. Dry the filter with its contents at 105° C. either in the funnel in which the operation was conducted or on a watch glass. It is advisable to protect the sample from dust by placing a large filter over the material.

9. Remove as much of the precipitate as possible from the filter, placing the silver chloride on a 4-inch square of glazed paper.

10. Ignite the filter, allowing the ash to drop into a weighed porcelain crucible. Add a drop of nitric acid and a drop of hydrochloric acid to react with any reduced silver. Place the silver salt (on the glazed paper) in the crucible and gently heat to 130–150° C. to expel water. If the AgCl appears dark, moisten with HCl and again apply heat to expel the free acid.

11. Cool in a desiccator.

12. Weigh as silver chloride. (wt. crucible+AgCl)−wt. crucible=wt. AgCl. The compound contains 24.74% of chlorine.

$$AgCl \times 0.2474 = Cl.$$

13. Calculate the per cent chlorine from the weight of sample taken.

Gooch Crucible Method.—8ᵃ. Prepare a Gooch crucible filter with a moderately thick asbestos mat and wash thoroughly with distilled water containing 1 ml. nitric acid per 100 ml. of water.

9ᵃ. Dry the crucible with mat in an oven at 100° C., then heat gently over a free blue flame. Cool in desiccator and weigh.

10ᵃ. Wash the silver chloride, first by decantation, then transfer to the Gooch crucible, which has been placed in position on a suction flask. Gentle suction is applied and the precipitate is washed free of chloride by repeated additions of the wash water containing the nitric acid.

11ᵃ. Place the crucible in an oven for 15 minutes or more and dry at 105° C. Now heat to about 130–150° C. to expel water. Cool in a desiccator.

12ᵃ. Weigh. The weight in excess of that due to the crucible is due to silver chloride.

13ᵃ. Calculate per cent chlorine as stated under the "filter paper method," 12 and 13.

NOTE.—Instead of a Gooch crucible a Jena glass crucible or a Koenig porcelain filter crucible may be used.

The silver chloride may be removed from the crucible by adding a piece of zinc and dilute sulfuric acid to the residue. AgCl is soluble in ammonium hydroxide solution. Concentrated hydriodic acid (sp. grav. 1.70) is an excellent agent for the removal of AgCl, AgBr, or AgI from filter crucibles (Caley and Burford, Ind. Eng. Chem., Anal. Ed. 8, 67, 1936).

Owing to the slight solubility of AgCl it has been recommended to wash first with water containing $AgNO_3$ (0.05 g. per liter), then with 1% soln. of HNO_3 and finally twice with pure water.

VOLUMETRIC METHODS

DETERMINATION OF CHLORINE IN ACID SOLUTION, SILVER THIOCYANATE-FERRIC ALUM METHOD

The method, devised by Volhard,[9] is applicable to titration of chlorine in acid solutions, a condition frequently occurring in analysis, where the Silver-Chromate Method of Mohr cannot be used. The method is based on the fact that when solutions of silver and an alkali thiocyanate are mixed in presence of a ferric salt, the thiocyanate has a selective action towards silver, combining with this to form thiocyanate of silver, any excess of that required by the silver reacting with the ferric salt to form the reddish-brown ferric thiocyanate, which color serves as an indication of the completion of the reaction. An excess of silver nitrate is added to the nitric acid solution containing the chloride, AgCl filtered off, and the excess of silver titrated with the thiocyanate in presence of the ferric salt.

Copper (up to 70%), arsenic, antimony, cadmium, bismuth, lead, iron, zinc, manganese, cobalt, and nickel do not interfere, unless the proportion of the latter metals is such as to interfere by intensity of the color of their ions.

Preparation of Special Reagents. *N/10 Ammonium or Potassium Thiocyanate Solution.*—About 8 grams of ammonium or 10 grams of potassium salt are dissolved in water and diluted to one liter. The solution is adjusted by titration against the N/10 silver nitrate solution. It is advisable to have 1 ml. of the thiocyanate equivalent to 1 ml. of the silver nitrate solution. Owing to the deliquescence of the thiocyanates the exact amount for an N/10 solution cannot be weighed.

N/10 Silver Nitrate.—This solution contains 10.788 grams Ag or 16.989 grams $AgNO_3$ per liter. The silver nitrate salt, dried at 120° C., or pure metallic silver may be taken, the required weight of the latter being dissolved in nitric acid and made to volume, or 17.1 grams of the salt dissolved in distilled water and made to 1000 ml. The solution is adjusted to exact decinormal strength by standardizing against an N/10 sodium chloride solution, containing 5.846 grams of pure NaCl per liter.

Ferric Indicator.—Saturated solution of ferric ammonium alum. Should this not be available, $FeSO_4$ may be oxidized with nitric acid, and the solution evaporated with an excess of H_2SO_4 to expel the nitrous fumes. A 10% solution is desired. Five ml. of either of these reagents are taken for each titration.

Pure Nitric Acid.—This should be free from the lower oxides of nitrogen. Pure nitric acid is diluted to contain about 50% HNO_3, and boiled until perfectly colorless. The reagent should be kept in the dark. Dilute nitric acid does not interfere with the method.

Procedure.—To the solution, containing 0.003 to 0.35 gram chlorine, in combination as a chloride, is added sufficient of the pure HNO_3 to make the solution acid and about 5 ml. in excess. To the solution, diluted to about 150 ml., is added an excess of standard silver nitrate reagent. The precipitated AgCl

[9] Liebig's Ann. d. Chem., 190, 1; Sutton, "Volumetric Analysis"; Z. anorg. Chem., 63, 330, 1909.

is filtered off and washed free of silver nitrate. The filtrate and washings are combined and titrated with standard thiocyanate.[10]

The filtrate from the precipitated chloride is treated with 5 ml. of the ferric solution,[11] and the excess silver determined by addition of the thiocyanate until a permanent reddish-brown color is produced. Each addition of the reagent will produce a temporary reddish-brown color, which immediately fades as long as silver uncombined as thiocyanate remains. The trace of excess produces ferric thiocyanate, the reddish-brown color of this compound being best seen against a white background. From this titration the amount of silver nitrate used by the chloride is ascertained.

One ml. N/10 $AgNO_3$ = 0.003546 gram Cl or 0.005845 gram NaCl.

Titration without Filtering off the Silver Chloride.

If 1 ml. of nitrobenzene is added for each 50 mg. of chloride, the solution may be titrated by thiocyanate without filtering off the silver chloride.[12] The solution containing 48 to 260 mg. of chloride in a volume of 25–50 ml. acidified with 8–10 drops of conc. HNO_3 is treated with excess of silver nitrate and the amount of nitrobenzene above stated, shaken in a glass-stoppered bottle until spongy flakes of AgCl are obtained, and then titrated with thiocyanate after adding ferric alum indicator.

VOLUMETRIC DETERMINATION OF CHLORINE IN A NEUTRAL SOLUTION, SILVER CHROMATE METHOD

The method, worked out by Fr. Mohr, is applicable for determination of chlorine in water or in neutral solutions containing small amounts of chlorine; the element should be present combined as a soluble chloride. Advantage is taken of the fact that silver combines with chlorine in presence of a chromate, Ag_2CrO_4 being decomposed as follows: $Ag_2CrO_4 + 2NaCl = 2AgCl + Na_2CrO_4$. When all the chlorine has gone into combination as AgCl, an excess of K_2CrO_4 immediately forms the red Ag_2CrO_4,[13] which shows the reaction of $AgNO_3$ with the chloride to be complete.

Reagents. ***Tenth Normal Silver Nitrate Solution.***—Theoretically 16.989 grams $AgNO_3$ per liter are required. In practice 17.1 grams of the salt are dissolved per 1000 ml. and the solution adjusted against an N/10 NaCl solution containing 5.846 grams NaCl per liter.

Potassium Chromate.—Saturated solution.

Procedure.—To the neutral solution are added 2 or 3 drops of the potassium chromate solution. A glass cell [14] (or a 50-ml. beaker) is filled to about 1 cm.

[10] Time is saved by filtering, through a dry filter paper, only a portion of the mixture made to a definite volume, and titrating an aliquot portion. The first 10–15 ml. of the filtrate are rejected.

[11] Upon addition of the ferric solution no color should develop. If a reddish or yellowish color results, more nitric acid is required to destroy this. The amount of nitric acid does not affect results when within reasonable limits.

[12] Method of J. R. Caldwell and H. V. Moyer, Ind. Eng. Chem., Anal. Ed. 7, 38 (1935).

[13] Six parts Ag_2CrO_4 dissolved in 100,000 parts H_2O at 15.5° C.—W. G. Young, Analyst, 18, 125.

[14] Depré, Analyst, 5, 123; also, Systematic Handbook of "Volumetric Analysis," F. A. Sutton.

in depth with water tinted to the same color as the solution being titrated. The cell is placed on a clear glass plate half covering the casserole containing the sample. The standard silver solution is now added to the chloride solution from a burette until a faint blood-red tinge is produced, the red change being easily detected by looking through the blank, colored cell.

One ml. N/10 $AgNO_3$ = 0.003546 gram Cl.

NOTES.—Chlorides having an acid reaction ($AlCl_3$) are treated with an excess of neutral solution of sodium acetate and then titrated with silver nitrate.

Elements whose ions form colored solution with chlorine are precipitated from the solution by sodium hydroxide or potassium carbonate, and the filtrate, faintly acidified with acetic acid, is titrated as usual.

Free hydrochloric acid is neutralized with ammonium hydroxide and titrated.

It is advisable to titrate the sample under the same conditions as those observed during standardization. The solution should be kept to small bulk and low temperature for accuracy on account of the solubility of the silver chromate.

Free chlorine should be converted to a chloride before titration. This may be accomplished, as stated under preparation of the sample, by boiling with ammonium hydroxide. Free chlorine may be determined by sweeping the gas, by means of a current of air, into a solution containing potassium iodide, the liberated iodine titrated by N/10 thiosulfate, $Na_2S_2O_3$, and the equivalent chlorine estimated.

ADSORPTION INDICATOR METHOD (FAJANS)

A 0.2% alcoholic solution of fluorescein, or a 0.2% aqueous solution of sodium fluoresceinate (Uranin) is used as indicator.[15] 1.5–6 drops of the indicator are added per 10 ml. of the neutral halide solution. Titration is made with standard silver nitrate until the precipitate suddenly appears reddish. In more dilute solutions the color change and the coagulation coincide. This indicator is not satisfactory for solutions of chloride content less than 0.005 N, as for example drinking water. With *dichlorfluorescein* as indicator solutions 0.025 N in chloride may be titrated satisfactorily down to pH 4, or 0.0005 N solutions at pH 7.[16] Not more than 2–4 drops of a 0.1% aqueous solution of the sodium salt of dichlorfluorescein need be used per 50 ml. of a very dilute chloride solution; in other cases 2 drops of indicator are added per 10 ml. of halide solution. In the very dilute solutions the end-point is given by a distinct change to an orange shade. The rose or reddish tints appear beyond the endpoint.[17]

VOLUMETRIC DETERMINATION OF FREE CHLORINE

The determination depends upon the reaction Cl+KI=KCl+I. The iodine liberated by the chlorine is titrated with $Na_2S_2O_3$ and the equivalent Cl calculated.

Procedure.—A measured amount of the chlorine water is added to a solution of potassium iodide in a glass-stoppered bottle by means of a pipette,

[15] K. Fajans and H. Wolf, Z. anorg. allgem. Chem., 137, 221 (1924).

[16] I. M. Kolthoff, W. M. Lauer and C. J. Sunde, J. Am. Chem. Soc., 51, 3273 (1929).

[17] For full details regarding all applications of adsorption indicators see the chapter by Fajans in Neuere Massanalytische Methoden, Vol. XXXIII, Die Chemische Analyse, Margosches-Böttger, F. Enke, Stuttgart, 1937. English translation published by D. Van Nostrand Co., New York.

the delivery tip of which is just above the surface of the iodide solution. The bottle is then closed and the contents vigorously shaken. The liberated iodine is titrated with tenth-normal sodium thiosulfate ($2Na_2S_2O_3+I_2=2NaI+Na_2S_4O_6$). When the yellow color of the iodine has become faint, a little starch solution is added and the titration completed to the fading out of the blue color.

One ml. N/10 $Na_2S_2O_3$ = 0.003546 gram Cl.

DETERMINATION OF HYPOCHLOROUS ACID IN THE PRESENCE OF CHLORINE

The determination depends upon the reactions:

$$2KI+HOCl=KCl+KOH+I_2 \text{ and } 2KI+Cl_2=2KCl+I_2.$$

The alkali liberated by hypochlorous acid and the total iodine are determined and the calculations made for each of the constituents.

Procedure.—A measured volume of N/10 HCl is added to a potassium iodide solution. To this the sample containing the hypochlorous acid and chlorine are added. The liberated iodine is titrated with N/10 $Na_2S_2O_3$. (The addition of starch is omitted.) The colorless solution is treated with methyl orange indicator and the excess of hydrochloric acid is titrated with N/10 NaOH. The potassium hydroxide, produced by the action of the hypochlorous acid upon the iodide, requires half as much acid for neutralization as the volume of thiosulfate required by the iodine set free by the hypochlorous acid.

Calculation.—The ml. back titration with NaOH are subtracted from the total ml. of HCl taken = ml. HCl required by NaOH liberated by HOCl = A. Then $2A$ ml. = ml. $Na_2S_2O_3$ required by the I liberated by HOCl. Ml. $A\times0.005247$ = gram HOCl. The total $Na_2S_2O_3$ titration minus $2A$ ml. (due to the iodine liberated by HOCl) = ml. $Na_2S_2O_3$ that are required by the iodine liberated by chlorine. The ml. thus required multiplied by 0.003546 = grams chlorine in the sample taken.

GRAVIMETRIC DETERMINATION OF CHLORIC ACID, $HClO_3$, OR CHLORATES, BY REDUCTION TO CHLORIDE AND PRECIPITATION AS SILVER CHLORIDE

Reduction of the Chlorate.—Among the methods of reduction of chlorates the following deserve special mention: 1. *Reduction with Sulfurous Acid.*[18] 2. Ferrous sulfate. 3. Zinc.

1. About 0.2 to 0.5 gram of the salt is dissolved in 100 ml. of distilled water and either SO_2 gas passed into the solution or sulfurous acid in solution added in excess. The solution is now boiled to expel SO_2 and the chloride precipitated as AgCl in presence of free nitric acid.

2. The sample in 100 ml. of distilled water is treated with 50 ml. of crystallized ferrous sulfate (10% solution), heated to boiling, with constant stirring, and then boiled for fifteen minutes. Nitric acid is added to the cooled solution, until the deposited basic ferric salt is dissolved. The chloride is now precipitated as AgCl, as usual.

[18] Blattner and Brassuer, Chem. Zeit. Rep., 24, 793, 1900.

3. The dilute chlorate solution is treated with acetic acid until it reacts distinctly acid. An excess of powdered zinc is now added and the solution boiled for an hour. Nitric acid is added to the cooled solution in sufficient quantity to dissolve the zinc remaining. The solution is filtered, if necessary, and the chloride precipitated as usual.

Factors. $AgCl \times 0.855 = KClO_3$, or $\times 0.2474 = Cl$.

NOTE.—In absence of cyanides, carbonates and acids decomposed and volatilized by hydrochloric acid, or oxides, hydroxides and substances other than chlorates that may be decomposed or acted upon by this acid, evaporation of the salt with HCl and ignition of the residue, or addition of an excess of ammonium chloride,[10] and subsequent heating will give a residue of chloride, which may be determined as usual and the equivalent chlorate calculated. Method by L. Blangey.

The methods may be used in determining chlorates in presence of perchlorates, only the former being reduced to chlorides. Outline of the procedure is given later.

GRAVIMETRIC DETERMINATION OF PERCHLORIC ACID BY REDUCTION TO CHLORIDE

A perchlorate ignited with about four times its weight of ammonium chloride in a platinum dish may be decomposed to chloride. A second treatment is usually necessary to change the salt completely. Platinum appears to act as a catalyser, so must be added in solution if a porcelain crucible is used.

Procedure.—About 0.2 to 0.5 gram of potassium perchlorate is intimately mixed with about 2 grams of ammonium chloride in a platinum crucible, the latter then covered with a watch-glass and the charge ignited gently for one and a half to two hours, the temperature being below the fusing-point of the residual chloride (otherwise the platinum would be attacked). A second addition of ammonium chloride is made and the mix again heated as before. The resulting chloride may now be determined as usual.

Factors. $AgCl \times 0.9666 = KClO_4$, $\times 0.2474 = Cl$.

DETERMINATION OF CHLORATES AND PERCHLORATES IN PRESENCE OF ONE ANOTHER

(1) A portion of the sample is treated with about twelve times its weight of ammonium chloride in a platinum dish (or in a porcelain dish with the addition of 1 ml. of hydroplatinic acid), and the mixture heated according to the procedure given for perchloric acid. The resulting chloride is determined as usual. This is the total chlorine in the sample.

(2) In a second portion the chlorate is reduced by means of SO_2 or $FeSO_4$, according to directions given for determination of chloric acid, and chlorine determined. The chlorine of this portion is subtracted from the total chlorine, the difference multiplied by $3.9076 = KClO_4$. The chlorine of the second portion multiplied by $3.4563 = KClO_3$, or AgCl in (2) subtracted from AgCl of (1) and the difference multiplied by $0.9666 = KClO_4$. AgCl of (2) multiplied by $0.855 = KClO_3$.

[10] Perchlorates are decomposed by ignition with NH_4Cl in presence of platinum.

DETERMINATION OF HYDROCHLORIC, CHLORIC, AND PERCHLORIC ACIDS IN THE PRESENCE OF ONE ANOTHER

(1) **Total Chlorine.**—If the determination is made in the valuation of niter a 5-gram sample is fused with about three times its weight of alkali carbonate [20] or calcium hydroxide,[21] in a platinum dish, whereby all the chlorine compounds are converted to chlorides. If the compounds are present as alkali salts, fusion with ammonium chloride in a platinum dish may be made and the total chlorides determined after dissolving the residue in nitric acid.

(2) **Chloride and Chlorate.**—If the estimation is being made in niter, 5 grams of the salt are treated with 10 grams of zinc dust (Cl-free) in presence of 150 ml. of 1% acetic acid. The solution is boiled for half an hour, filtered, and the chloride determined. In a mixture of alkali salts of hydrochloric, chloric, and perchloric acids, reduction may be accomplished by passing in SO_2 gas or by adding ferrous sulfate and boiling according to directions given for the determination of chlorate. The chloride now present in the residue is due to the reduced chlorate and to the original chloride of the sample.

(3) The chloride of the sample is determined by acidifying the salt with nitric acid (cold) and precipitating as AgCl.

Perchlorate.—The chloride and chlorate in terms of chlorine are subtracted from total chlorine of (1) and multiplied by the factor for the salt desired.

Chlorate.—The chlorine of (3) is subtracted from chlorine of (2) and multiplied by the factor for the compound desired.

Chloride.—The AgCl of (3) is multiplied by the appropriate factor.

Factors. $AgCl \times 0.2474 = Cl$, or $\times 0.2544 = HCl$, or $\times 0.4078 = NaCl$, or $\times 0.5201 = KCl$.

$AgCl \times 0.855 = KClO_3$, or $\times 0.9666 = KClO_4$.

$Cl \times 3.4563 = KClO_3$, or $\times 3.9076 = KClO_4$, or $\times 2.1027 = KCl$, or $\times 3.0023 = NaClO_3$ or $\times 3.4535 = NaClO_4$, or $\times 1.6486 = NaCl$.

DETERMINATION OF CHLORINE, BROMINE, AND IODINE IN THE PRESENCE OF EACH OTHER

The procedure is Bekk's modification of Baubigny's method.[22]

Procedure.—The halogens are precipitated with an excess of silver nitrate, filtered onto asbestos or glass wool, washed, dried, and weighed as total halogens as silver salts. A second portion is precipitated and the moist, washed silver salts (0.3 to 0.4 gram) are treated with a solution of 2 grams of potassium dichromate in 30 ml. of concentrated sulfuric acid at 95° C., and digested for thirty minutes. By this procedure the iodine is oxidized to iodic acid (HIO_3) and chlorine together with bromine is liberated in form of the free halogen. Toward the end of the reaction a stream of air is led through the solution to remove any chlorine and bromine. This is now diluted to 300 to 400 ml., filtered, and the iodic acid reduced by adding, drop by drop, with constant stirring, a concentrated solution of sodium sulfite, Na_2SO_3, until a faint odor of SO_2 remains after standing ten minutes. (Under certain conditions an

[20] Mennick, Chem. Zeit. Rep., 22, 117, 1898.
[21] Blattner and Brasseur, Chem. Zeit. Rep., 24, 793, 1900.
[22] Julius Bekk, Chem. Ztg., 39, 405–6, 1915. C. A., 9, 2042, 1915.

excess may result in a partial reduction of the silver iodide.) The precipitated silver salt is filtered, washed with hot, dilute nitric acid, dried and weighed as AgI. The filtrate containing the silver, formerly with the chlorine and bromine, is treated with potassium iodide in sufficient amount to completely precipitate the silver as AgI. This is filtered, washed and weighed. From the three weights the chlorine, bromine and iodine can be easily calculated.

NOTE.—Bekk claims an accuracy within less than 0.15%.

DETERMINATION OF FREE HYDROCHLORIC ACID

In absence of other free acids, hydrochloric acid may be accurately determined by titration with standard alkali. Details for the volumetric analysis of muriatic acid in presence of commonly occurring impurities are given in Volume II in the chapter on Acids.

One ml. N/1 NaOH = 0.03647 g. HCl.

DETERMINATION OF CHLORIDE AND CYANIDE IN PRESENCE OF ONE ANOTHER

The cyanide is determined by Liebig's method described on page 661. To the neutral solution is added sufficient N/10 silver nitrate to combine with all of the cyanide and chloride present and an excess. The solution is acidified with nitric acid and diluted to a definite volume and a portion filtered through a dry filter. A portion of the filtrate, an aliquot of the whole, is titrated with standard thiocyanate solution (page 271) using ferric alum indicator and the excess of the $AgNO_3$ added thus ascertained. From this the amount combined with the CN and Cl is known. The equivalent required by the cyanide is deducted, the difference being due to the chloride present in the solution.

1 ml. N/10 $AgNO_3$ = 0.005204 g. CN, or 0.013023 g. KCN, or 0.003546 g. Cl or 0.005845 g. NaCl, or 0.007455 g. KCl.

DETERMINATION OF CHLORIDE, CYANIDE AND THIOCYANATE IN PRESENCE OF ONE ANOTHER

The cyanide is determined by the method of Liebig described on page 661, and the equivalent $AgNO_3$ required recorded = A.

An excess of N/10 $AgNO_3$ over that required by CN, CNS and Cl is added and the solution acidified with nitric acid. After making to a definite volume, the solution is filtered through a dry filter, the residue being saved. A portion of the filtrate, an aliquot of the whole solution, is titrated with standard thiocyanate solution using ferric alum indicator (see page 271), the excess of $AgNO_3$ is calculated. The amount combining with CN, CNS and Cl is now known = B.

The silver salts on the filter paper are washed with water and transferred by means of conc. nitric acid to a flask and boiled for an hour. The cyanide

and thiocyanate are decomposed and dissolve, while the silver chloride remains unchanged. The sulfuric acid formed by oxidation of the thiocyanate is precipitated by barium nitrate (as $BaSO_4$). Without removing the precipitates AgCl and $BaSO_4$ the silver nitrate in this solution is determined by Volhard's method (page 271) and the $AgNO_3$ required by thiocyanic acid and cyanide thus ascertained = C.

By deducting the $AgNO_3$ of (A) from (C) the silver nitrate required by thiocyanic acid is determined.

Deducting the $AgNO_3$ required by CN and CNS (C) from the total $AgNO_3$ required by CN, CNS and Cl (B) the amount required by chlorine is obtained.

We now have the silver nitrate equivalent of Cl, CN, CNS.

N/10 $AgNO_3$ = 0.005204 g. CN, or 0.005808 g. CNS or 0.003546 g. Cl.

NOTE.—In the analysis of compounds containing hypochlorites and chlorides, the conversion of hypochlorites to chlorides by heating with hydrogen peroxide is a great convenience.

For instance in the analysis of bleach liquors, washes, etc., the (OCl) and Cl may be very easily and quickly determined by titrating an aliquot with As_2O_3 and then a similar aliquot with $AgNO_3$ after converting all the OCl to Cl by warming with H_2O_2.

EVALUATION OF BLEACHING POWDER, CHLORIDE OF LIME, FOR AVAILABLE CHLORINE

When chloride of lime is treated with water, it is resolved into calcium hypochlorite, $Ca(OCl)_2$, and calcium chloride, $CaCl_2$. The calcium hypochlorite constitutes the bleaching agent. The technical analysis is confined to the determination of available chlorine, which is expressed as percentage by weight of the bleaching powder.

Procedure.—Ten grams of the sample are washed into a mortar and ground with water, the residue allowed to settle and the supernatant liquor poured into a liter flask. The residue is repeatedly ground and extracted with water until the whole of the chloride is transferred to the flask. The combined extracts are made up to 1000 ml.

To 50-ml. portions (0.5 gram) of the solution, 3 to 4 grams of solid potassium iodide and 100 ml. of water are added and the solution acidified with acetic acid. Iodine equivalent to the available chlorine is liberated.[23] This is titrated with N/10 arsenious acid.

[23] This iodine is liberated, in all probability, by the oxygen present in NaOCl.

One ml. N/10 arsenious acid = 0.003546 gram Cl. This multiplied by 200 = % Cl.

NOTE.—In France the strength is given in Gay-Lussac degrees, e.g., liters of gas evolved by 2 kilograms of bleaching powder, 0° C. and 760 mm. 100° = 31.78% Cl.

METHOD FOR THE ANALYSIS OF LIQUID BLEACH

Special Reagents Required.

Reagent 12. Barium Chloride (100 g.p.l. $BaCl_2 \cdot 2H_2O$).
Reagent 37. Methyl Orange Indicator.
Reagent 41. Phenolphthalein Indicator.
Reagent 62. N/10 Sodium Thiosulfate.
Reagent 64. Starch Indicator.
Reagent 110. N/10 Hydrochloric Acid.

Preparation of Sample.—For strong solutions of bleach, pipette 10 ml. into a 250-ml. graduated flask containing about 100 ml. of distilled water, keeping the tip of the pipette beneath the surface of the water. Dilute to the mark and mix thoroughly. Use an aliquot portion for the determination of available chlorine. For the other determinations and for available chlorine in weak bleach (below 35.0 g.p.l. available chlorine), use the sample as received.

"Available Chlorine."—For available chlorine the size of the sample should be such that it will titre about 40.0 ml. of N/10 $Na_2S_2O_3$.

Dissolve 2–3 grams of potassium iodide crystals in 50 ml. of distilled water in a 250-ml. Erlenmeyer flask. Introduce the sample under the surface of the solution and acidify slightly with acetic acid. Titrate with N/10 sodium thiosulfate (Reagent 62) until the yellow color of iodine is nearly destroyed. Add 5 ml. of starch solution (Reagent 64) and titrate until the blue color entirely disappears.

$$\frac{\text{ml. N/10 } Na_2S_2O_3 \times 3.546}{\text{ml. of sample}} = \text{g.p.l. "available" chlorine,}$$

$$\frac{\text{ml. N/10 } Na_2S_2O_3 \times 0.3546}{\text{wt. of sample}} = \text{\% "available" chlorine.}$$

Total Na_2O.—Pipette sufficient sample, so that the total titre will be at least 10 ml. of N/10 HCl, into a 150-ml. Erlenmeyer flask, dilute with 25 ml. of distilled water and add 25 ml. of conc. NH_4OH. Boil until the odor of

NH_4OH has entirely disappeared. Cool and titrate with N/10 HCl (Reagent 110) using methyl orange (Reagent 37) as the indicator.

$$\frac{\text{ml. N/10 HCl}\times 3.1}{\text{ml. of sample}} = \text{g.p.l. } Na_2O,$$

$$\frac{\text{ml. N/10 HCl}\times .31}{\text{wt. of sample}} = \%\ Na_2O.$$

Sodium Hydroxide (NaOH).—Proceed as directed for total Na_2O, using the same size sample, until ready to titrate. Transfer to a 400-ml. beaker, add 50 ml. of $BaCl_2$ (Reagent 12) and 10 drops of phenolphthalein (Reagent 41), stir well and titrate with N/10 HCl (Reagent 110) until the pink color disappears.

$$\frac{\text{ml. N/10 HCl}\times 4.0}{\text{ml. of sample}} = \text{g.p.l. NaOH},$$

$$\frac{\text{ml. N/10 HCl}\times .4}{\text{wt. of sample}} = \%\ \text{NaOH}.$$

Sodium Carbonate (Na_2CO_3).

$$\frac{(\text{N/10 HCl titre for } Na_2O - \text{N/10 HCl titre for NaOH})\times 5.3}{\text{ml. of sample}} = \text{g.p.l. } Na_2CO_3,$$

$$\frac{(\text{N/10 HCl titre for } Na_2O - \text{N/10 HCl titre for NaOH})\times .53}{\text{wt. of sample}} = \%\ Na_2CO_3.$$

NOTE.—1. The Na_2CO_3 may be determined on the CO_2 machine (T. S. P. method 533) after treatment with NH_4OH to destroy hypochlorites as described under NaOH.

2. N/10 H_2SO_4 may be used in place of N/10 HCl but the results will not be as accurate, due to the $BaSO_4$ precipitate present in the determination of NaOH. This precipitate occludes part of the NaOH, making the titration low.

COLORIMETRIC ESTIMATION OF CHLORINE IN WATER

The procedure makes use of the fact that when water containing free chlorine is treated with ortho-tolidine reagent, a definite color is obtained. Small amounts of free chlorine give a yellow, and larger amounts an orange color. The quantitative estimation is carried out by comparing this color with color standards representing definite amounts of free chlorine.

The set as supplied consists of five chlorine color standards with the values 0.1, 0.2, 0.3, 0.4 and 0.5 parts of chlorine per million, made up in sealed 25 ml. bottles; 1–25 ml. testing bottle; 50 ml. of ortho-tolidine reagent; and a calibrated 0.5 ml. pipette with nipple; all compactly arranged in a portable case of sturdy construction, 8½ inches long, 4½ inches wide and 6 inches high.

A determination of free chlorine is made as follows: Rinse the testing bottle with the water to be tested. Place about 25 ml. of the water in the bottle and add 0.5 ml. of ortho tolidine reagent by means of the pipette. Stopper tightly and shake well. Allow the solution to stand at least 5 minutes and compare the color developed with that of the chlorine color standards. The value can then be read off directly from the standards.

Water having over 0.5 parts per million of free chlorine should be diluted with chlorine-free water, preferably distilled. For example, suppose a water contained 0.8 parts per million of free chlorine. Equal volumes of distilled water and the water to be tested should be thoroughly mixed and the determination carried out as described above. The diluted sample will be found to contain 0.4 parts per million of free chlorine. This value would then be multiplied by 2 to give the actual chlorine content. Higher values would require further dilution and this dilution would determine the factor by which the actual reading is multiplied.

In the sterilization of drinking water with chlorine, the usual *dosage* is from 0.25 to 0.50 parts per million, or 2 to 4 pounds per million gallons. Sometimes in a polluted or suspicious water, as much as 1.0 part per million is used, but this may cause a very strong taste. The dosage is affected by the presence of organic matter or oxidizable salts and by the hydrogen ion concentration, since oxidation results more quickly in the presence of free carbonic acid. The practical method is to so regulate the chlorine dosing device that frequent samples, taken at a point in the distribution system that allows for a 5 minute contact period, show a residual chlorine value of 0.1 to 0.2 parts per million.

Tropaolin OO adsorption indicator is useful in titration of halogens with $AgNO_3$. Five drops of indicator (0.5% in water and ethanol 1 : 1) give a cream color during titration changing definitely pink at end-point.

Para-aminodimethyl-aniline Test for Halogens [24]

To Make the Test.—Two or three drops of the reagent should be added to five ml. of distilled water and the solution to be tested slowly added. Only enough of the solution to be tested should be added that will produce a pink color, or other confusing results are apt to ensue.

For example: If a 0.01 per cent solution of bromine is added, a drop at a time, to five ml. of the reagent, the following colors will appear in turn: pink, red, purple, violet-red, green, brown, and yellow, all definite colors formed by the successive halogenation of the benzene nucleus and the methyl side chains in quite a complex manner.

The reagent when properly used will detect:

1 part bromine in 1,300,000 parts of water,
1 part chlorine in 65,000 parts of water,
1 part iodine in 400,000 parts of water.

Note. **To Prepare the Reagent.**—Dissolve five grams of para-aminodimethylaniline in 100 ml. of absolute alcohol. The alcohol is used as the solvent with preference over water because it permits less decomposition.

[24] Ind. Eng. Chem., Anal. Ed. 3, 225, 1931.

CHROMIUM [1]

Cr, ***at.wt.*** **52.01;** ***sp.gr.*** **7.1;** ***m.p.*** **1615° C.;** ***b.p.*** **2200° C.;** ***oxides,*** **CrO_3; Cr_2O_3, CrO,**

Chromium occurs in nature in combined state, more generally in rocks of high magnesia and low silica content. It is found associated with iron, aluminum, calcium, copper, magnesium. The minerals chromite, chrome iron, $FeO \cdot Cr_2O_3$, and crocoisite, $PbCrO_4$, are of commercial importance.

Chromium is used in alloys, in steel, in paint pigments, in chrome plating and has accordingly received much attention regarding its properties and chemical reactions with methods of determination.

DETECTION

Chromium is precipitated by ammonium hydroxide as bluish-green, $Cr(OH)_3$, along with the hydroxides of iron and aluminum (members of previous groups having been removed). The chromic compound is oxidized to chromate by action of chlorine, bromine, sodium peroxide, or hydrogen peroxide added to the substance containing an excess of caustic alkali. The chromate dissolves and is thus separated from iron, which remains insoluble as $Fe(OH)_3$. The alkali chromates color the solution yellow .

Barium acetate or chloride added to a neutral or slightly acetic acid solution of a chromate precipitates yellow barium chromate, $BaCrO_4$. Addition of ammonium acetate to neutralize any free inorganic acid aids the reaction.

Lead acetate produces a yellow precipitate with chromates, in neutral or acetic acid solutions.

Mercurous nitrate or silver nitrate gives red precipitates with chromates.

Hydrogen peroxide added to a chromate and heated with an acid, such as sulfuric, nitric, or hydrochloric, will form a greenish-blue-colored solution. Chromates are reduced by hydrogen peroxide in acid solution, the action being reversed in alkaline solution.

Reducing agents, hydrogen sulfide, sulfurous acid, ferrous salts, alcohol form green chromic salts when added to chromates in acid solution.

Ether shaken with a chromate to which nitric acid and hydrogen peroxide are added is colored a transient blue by the unstable perchromic acid, which

[1] Vauquelin discovered chromium in crocoisite in 1797.

soon decomposes into chromic salt with evolution of oxygen and fading of the blue color.

Diphenyl Carbazide Test.—To 5 ml. of the solution containing chromium as chromate, 2 drops of hydrochloric or acetic acid are added, and 1 drop of an acetic acid solution of diphenyl carbazide (0.2 gram $CO(NH \cdot NH \cdot C_6H_5)_2$ is dissolved in 5 ml. glacial acetic acid and diluted to 20 ml. with ethyl alcohol). A violet pink color is produced in presence of a chromate. Less than 0.0000001 gram chromium may be detected.

Chromic salts are bluish green; chromic acid is red; chromates, yellow; dichromates, red; chrome alum, violet.

The powdered mineral, containing chromium, when fused with sodium carbonate and nitrate, produces a yellow colored mass.

ESTIMATION

Among the substances in which chromium is determined are the following: Chrome iron or chromite, $Cr_2O_3 \cdot FeOMgO$; crocoisite, $PbCrO_4$; slags; chromic oxide, chrome green, in pigments; chromates and dichromates; chrome steel and ferro-chrome.

In analytical procedures chromium precipitates with iron and aluminum and causes difficulty in the determination of these two elements. In the iron determination by titration with $KMnO_4$, chromium, if present, is also reduced by zinc from a valence of three to a valence of two and is again oxidized to the trivalent form by $KMnO_4$, similar to the action with iron.‡ No reduction of trivalent chromium occurs with use of H_2S, SO_2 or $SnCl_2$, while iron is reduced.

Details of getting chromium products into solution follow. The attack with sodium peroxide is generally satisfactory. The methods for its determination seldom require preliminary separations.

PREPARATION AND SOLUTION OF THE SAMPLE

Although powdered metallic chromium is soluble in dilute hydrochloric or sulfuric acid, it is only slightly soluble in dilute or concentrated nitric acid. It is practically insoluble in aqua regia and in concentrated sulfuric acid. Chrome iron ore is difficult to dissolve. It is important to have the material in finely powdered form to effect a rapid and complete solution of the sample. An agate mortar may be used to advantage in the final pulverizing of the substance.

‡ At room temperature Cr^{III} is not reduced to Cr^{II} at 10° or below by Zn(Hg). At 100° $KMnO_4$ oxidizes Cr^{III} to Cr^{VI}.

General Procedures for Decomposition of Refractory Materials Containing Chromium.—The following fluxes may be used:

A. Fusion with $KHSO_4$ and extraction with hot dilute HCl. The residue fused with Na_2CO_3 and $KClO_3$, 3 : 1, or fusion with soda lime and $KClO_3$, 3 : 1.

B. Fusion with $NaHSO_4$ and NaF, 2 : 1.

C. Fusion with magnesia or lime and sodium or potassium carbonates, 4 : 1.

D. Fusion with Na_2O_2, or NaOH and KNO_3, or NaOH and Na_2O_2. Nickel, iron, copper, or silver crucibles should be used for *D*. Platinum may be used for *A*, *B*, or *C*.

Special Procedures. Materials High in Silica.—The finely ground sample, 1 to 5 grams, is placed in a platinum dish and mixed with 2 to 5 ml. concentrated sulfuric acid (1.84), and 10 to 50 ml. of conc. hydrofluoric acid added. The solution is evaporated to small volume on the steam bath and to SO_3 fumes on the hot plate. Sodium carbonate is added in sufficient amount to react with the free acid, and then an excess of 5 to 10 grams added and the mixture heated to fusion and kept in molten condition for half an hour. From time to time a crystal of potassium nitrate is added to the center of the molten mass until 1 to 2 grams are added. (*Caution*. Platinum is attacked by KNO_3, hence avoid adding a large amount at any one time.) Chromium and aluminum go into solution in the flux, but iron is thrown out as $Fe(OH)_3$. The cooled fusion is extracted with hot water and filtered from the iron residue. Chromium is in solution together with aluminum. If much iron is present it should be dissolved in a little hydrochloric acid and the solution poured into boiling 10% solution of potassium hydroxide, the cooled solution + $Fe(OH)_3$ precipitate is treated with hydrogen peroxide or sodium peroxide to oxidize any chromium that may have been occluded by the iron in the first precipitate. The mixture is again filtered and the combined filtrates examined for chromium.

Sodium Peroxide Fusion. Chrome Iron Ores.—One gram of finely pulverized ore is mixed with 8 grams of yellow sodium peroxide. (Fresh peroxide is best and fused in a nickel or iron crucible of 30 ml. capacity.) See p. 296 for detailed procedure. The cooled fusion is dissolved in a casserole with 100 ml. to 150 ml. of water, more peroxide being added to this solution if it appears purple. The excess of peroxide is decomposed by boiling the solution, and to the caustic solution free from peroxide is added 10 to 15 grams of ammonium carbonate or a sufficient quantity of the salt to neutralize four-fifths of the sodium hydroxide present in the solution, as the strong caustic would otherwise dissolve the filter. The solution is now filtered. The insoluble matter is treated on the filter with dilute sulfuric acid, 1 : 4. If a portion remains insoluble, it is an indication of incomplete decomposition of the ore, and this residue is again fused with peroxide and treated as above. The combined filtrates contain the chromium.

Since chromates are reduced in presence of free acid and peroxide, the latter should be expelled before making the solution acid.[1]

If the chromate is to be precipitated as $BaCrO_4$ or $PbCrO_4$, the solution should be acidified with hydrochloric acid. If the reduced solution is to be titrated with potassium permanganate, it is best to use sulfuric acid in neutralizing the caustic solution. Further directions will be given under the method chosen.

[1] See Separations.

Chrome ores may be readily decomposed by fusion of one part of the ore with 8 parts of Na_2O_2 in a nickel, iron or porcelain crucible. Five minutes is ample time instead of the 25 minutes given. (See Analysis of Chrome Ores—Determination of Chromium, by Cunningham and McNeill.)

Method for Solution of Iron and Steel.—See methods at close of chapter.

SEPARATIONS

Chromium, Iron, and Aluminum.—If chromium has been fused with sodium peroxide or carbonate containing a little potassium nitrate, and the fusion extracted with boiling water, most of the chromium goes into solution as a chromate, together with alumina, but some of the chromium is occluded by $Fe(OH)_3$. If the amount of the iron precipitate is appreciable, and warrants the recovery of occluded chromium, it is dissolved in hydrochloric acid and the iron reprecipitated by pouring into a solution of strong sodium hydroxide. Before filtering off the iron hydroxide, a little H_2O_2 is added to oxidize the Cr_2O_3, if accidentally present, and the solution boiled and filtered. The combined filtrates will contain all of the chromium and aluminum.

If chromium is present as a chromic salt, instead of a chromate, it is oxidized to the higher form by adding peroxide (H_2O_2 or Na_2O_2) to the alkaline solution. Bromine added to this solution or chlorine gas passed in will accomplish complete oxidation.[3] It must be remembered that in acid solutions hydrogen peroxide, sodium peroxide, or nitrites will cause reduction of chromates to chromic salts (exception, see method for solution of steel), so that these should be boiled out of the alkaline solution before making decidedly acid with hydrochloric or sulfuric acid. Since these are difficult, if not impossible, to expel completely from an alkaline solution, after boiling the strongly alkaline solution, dilute sulfuric acid is added until the solution acquires a permanent brown color (nearly acid), acid potassium sulfate, $KHSO_4$, is added, and the boiling continued.[4] This will decompose the bromates and expel bromine, etc., but will not cause the reduction of the chromate, as would a strong acid solution.

Separation of Chromium from Aluminum.—This separation is necessary if chromium is to be precipitated as $Cr(OH)_3$. The sodium chromate and aluminate solutions are made slightly acid with nitric acid and then faintly alkaline with ammonium hydroxide, $Al(OH)_3$ is precipitated and chromium remains in solution as a chromate.

[3] Br may be added and then NaOH to oxidize Cr and precipitate $Fe(OH)_3$.

Chromic oxide and most of its compounds, except chrome iron stone, may be decomposed by conc. HNO_3+KClO_3 (added in small portions). M. Gröger, Z. anorg. Chem., 81, 233–242, 1913.

[4] $KHSO_4$ will not cause reduction of chromates. A. Kurtenacker, Z. anal. Chem., 52, 401–407, 1913; Analyst, 38, 449, 387.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF CHROMIUM

PRECIPITATION OF CHROMIC HYDROXIDE AND IGNITION TO Cr_2O_3[5]

Chromium present as a chromic salt in solution, free from iron and aluminum or elements precipitated as hydroxides, is thrown out of solution by NH_4OH as $Cr(OH)_3$, the precipitate ignited to the oxide, Cr_2O_3,[6] and so weighed. The presence of hydrochloric acid or sulfuric acid does not interfere.

Reduction.—If the chromium is already present as the chromic salt, free from iron and alumina, it may be precipitated directly as the hydroxide by addition of ammonia; otherwise, if present as the chromate, as is the case when a separation from iron and alumina has been necessary, and in cases where the chromium has been brought into solution by fusion with an oxidizing reagent, reduction is necessary. This is accomplished by passing SO_2 or H_2S into the slightly acid solution of the chromate, or by adding alcohol to the hydrochloric acid solution and boiling until the solution appears a deep grass green. Twenty ml. of alcohol for every 0.1 gram of Cr has been found to be ample for this reduction. The SO_2 or H_2S should be expelled from solution by boiling, in case either has been used for reduction of the chromate.

Precipitation. *Ammonium hydroxide or ammonium sulfide is added in slight excess and the solution boiled for about ten minutes.*—The solution should be slightly alkaline (litmus), otherwise a few drops of ammonia should be added, but not a large excess; the solution will then settle out clear. A cloudy solution results from prolonged boiling when the solution has become acid; on the other hand, a large excess of ammonia will prevent complete precipitation of chromium and the filtrate will be colored pink or violet. *The chromic hydroxide is filtered off on a rapid filter paper.* Since the precipitate is apt to be gelatinous it is advisable to wash two or three times by decantation and several times on the paper. The well-drained precipitate and filter is ignited wet in a porcelain or platinum crucible, first over a low flame until the paper has been charred, then over a strong flame until the carbon has been burned away, the oxide is finally heated strongly in a dry hydrogen atmosphere, using a Rose crucible cover. The flame is turned off and the precipitate is allowed to cool to about 100° C. in hydrogen before the crucible is placed in a desiccator the green residue is weighed as Cr_2O_3.[7] Wt. of $Cr_2O_3 \times 0.6843 =$ wt. of chromium.

[5] *It is advisable to take such a weight of sample that the ignited* Cr_2O_3 *does not exceed 0.5 gram in weight.*

[6] *Cr_2O_3, mol.wt., 152; sp.gr., 5.21; m.p., 1900° C.;* insol. in H_2O, slightly sol. in acids, dark green hexagonal.

[7] Rothaug, Z. anorg. Chem., 84, 165 (1913–1914). Chromic oxide is partially oxidized to chromic chromate in air. Oxygen is most rapidly absorbed in the range 100–300° C.

DETERMINATION OF CHROMIUM AS BARIUM CHROMATE

Chromium, present as a chromate, is precipitated from a neutral or faintly acetic acid solution of an alkali chromate by addition of barium acetate or chloride. The $BaCrO_4$ is gently ignited and weighed. The solution should be free from sulfuric acid or sulfates.

Procedure.—The alkali chromate solution is neutralized with nitric acid or ammonia as the case may require, precautions for avoiding reduction having been observed as indicated under Preparation and Solution of the Sample. Ten ml. of $\frac{1}{2}$ N $BaCl_2$ or $Ba(C_2H_3O_2)_2$ (approx. 10% soln.) are added to the boiling solution for each 0.1 gram of chromium present. The reagent should be added in a fine stream or drop by drop to prevent occlusion of the reagent by the precipitate. The precipitated chromate is allowed to settle on the steam bath for two or three hours and then filtered into a weighed Gooch crucible and washed with 10% alcohol solution.[8] The precipitate is dried for an hour in the oven, then placed in an asbestos ring suspended in a large crucible with cover and thus heated over a low flame, gradually increasing the heat until the outer crucible becomes a dull red. The cover is removed and the heating continued for five minutes, or until the precipitate appears a uniform yellow throughout. High heating should be avoided. The cooled residue is weighed as $BaCrO_4$.

$$BaCrO_4 \times 0.2053 = Cr.$$

$$BaCrO_4 \times 0.3000 = Cr_2O_3.$$

$$BaCrO_4 \times 0.7665 = K_2CrO_4.$$

$$BaCrO_4 \times 0.5806 = K_2Cr_2O_7.$$

Notes.—If the precipitate on the sides of the crucible appears green, it is ignited until the green color disappears.

If sulfates are present, $BaSO_4$ will be precipitated; hence this method could not be used. In this case either reduction to the chromic salt and precipitation of chromium as $Cr(OH)_3$ or a volumetric procedure should be followed.

Oxidize chromium with an excess of hydrogen peroxide in alkaline solution, reduce in acid solution with ferrous sulfate and titrate with permanganate. Decomposition of hydrogen peroxide is accelerated by heat and by presence of sodium sulfate or ferric salts. Salts of nickel, cobalt, or manganese decompose H_2O_2 energetically and lower results are obtained. F. Bourin and A. Senechal. Compt. rend., **157**, 1528–31.

Mercurous Nitrate Method.—To the chromate solution (containing 0.2–0.5 g. Cr) heated to boiling is added 2 grams of Na_2CO_3 and then a saturated solution of pure mercurous nitrate in 1/10 soln. conc. HNO_3 *(free from nitrous oxides), added in slight* excess. The mixture is boiled until the brown precipitate changes to the orange crystalline form. The precipitate is filtered and washed with hot water, then ignited three hours over a Meeker burner until the weight is constant.

[8] If the filtrate appears yellow, chromate is indicated, the solution should be reduced and the chromium precipitated as $Cr(OH)_3$. If the filtrate is pink, it should be boiled until it appears green and $Cr(OH)_3$ precipitates. These precipitates should be included in the above calculation for chromium.

$BaCrO_4$, *mol.wt.*, 253.37; *sp.gr.*, 4.498; solubility per 100 ml. H_2O, $0.00038^{18°}$ and 0.0043 hot. Soluble in HCl and in HNO_3; yellow rhombic plates.

Procedure.—The solution containing the sample is nearly neutralized with sodium carbonate, the reagent being added until a slight cloudiness results. The solution is now cleared with a few drops of sulfuric acid, and then sufficient excess of a strong solution of sodium thiosulfate added to precipitate aluminum, chromium, manganese, etc. The precipitate is filtered off, dissolved in the least amount of dilute nitric acid, then filtered from the precipitated sulfur and diluted to 300 to 400 ml. Chromium is now oxidized by adding 10 ml. of 0.2% silver nitrate solution, about 10 grams each of ammonium nitrate and persulfate. After boiling for about twenty minutes, sufficient hydrochloric acid is added to decompose any permanganate present and to precipitate the silver, and a few ml. added in excess. The solution is again boiled for about ten minutes and then filtered. The filtrate is treated with a little sodium phosphate to repress the color of traces of iron that may be present and made to a definite volume.

The solution may now be compared with a standard solution containing the same amounts of acids, manganese, alumina, etc., as are present in the sample, tenth normal potassium dichromate being run into this standard solution until its color matches that of the sample. The burette reading is taken and the chromium calculated.

$$\text{One ml. of } N/10\ K_2Cr_2O_7 = 0.001734 \text{ gram Cr.}$$

NOTES.—Prolonged boiling after addition of hydrochloric acid to the solution of the chromate will cause its reduction. A green tint usually indicates that the chromate has been reduced.

The test may be carried on in the presence of sulfuric, hydrochloric, phosphoric hydrofluoric, and nitric acids. Alumina, manganese, and small amounts of iron do not interfere.

Organic matter should be destroyed by either calcining the sample or by oxidation by taking to fumes with sulfuric acid. The presence of this prevents precipitation of chromium.

COLORIMETRIC ESTIMATION OF SMALL AMOUNTS OF CHROMIUM WITH DIPHENYL CARBAZIDE

Diphenyl carbazide, $CO(NH \cdot NH \cdot C_6H_5)_2$, gives a violet color with chromic salts or chromates in acid solution, the intensity of the color being proportional to the concentration of the chromate. Less than 0.0001 milligram of chromium may be detected by this reagent. The following procedure may be used for determining traces of the element:

1 to 2 grams of the substance, which has been brought into solution with water or acid, is treated with an excess of sodium peroxide to oxidize chromium, and the solution filtered. The filtrate, concentrated to 75–80 ml., is acidified with hydrochloric acid, so that there is present about 5 ml. of free concentrated acid (sp. gr. 1.19) per 100 ml. of solution. The solution, transferred to a Nessler tube, is treated with 1 ml. of the reagent, and the color compared with standards containing the same reagents as the sample examined. A colorimeter may be used and comparison made with a standard according to details given for the colorimetric comparison of traces of lead or titanium.

Preparation of Diphenyl Carbazide Reagent.—One-tenth of a gram of the compound is dissolved in 10 ml. of glacial acetic acid and diluted to 100 ml. with ethyl alcohol.

Diphenyl carbazide may be made by heating a mixture of 15 grams of urea with 50 grams of phenyl hydrazine four hours, finishing at 155° C. The solid product is crystallized three times with alcohol. A light straw-colored product is obtained. A white product is obtained if the urea is cut down to 5 grams; the yield, however, is only 25% of that obtained by the first method and the compound possesses no advantages.

DICHROMATE-DIPHENYLAMINE METHOD FOR DETERMINING CHROMIUM IN IRON ORES AND ALLOYS

The method takes advantage of Knop's reaction with diphenylamine (Journal of the American Chemical Society, Feb., 1924) in titration of iron with potassium dichromate; here chromate is titrated with a solution of iron. The procedure is applicable to the determination of chromium in ores, ferrochrome, chrome steels and soluble chromates.

Reagents. ***Potassium Dichromate.***—0.1 N solution.

Ferrous Ammonium Sulfate or Ferrous Sulfate.—0.1 N solution.

Phosphoric-Sulfuric Acid.—150 ml. sulfuric acid (sp. gr. 1.84) and 150 ml. phosphoric acid (sp. gr. 1.70) diluted to 1000 ml. with water.

Diphenylamine Indicator.—One g. of the reagent dissolved in 100 ml. of sulfuric acid (sp. gr. 1.84). Use 4 drops (0.2 ml.). Deduct 0.1 ml. blank.

Sodium Peroxide.—Fresh powder.

Procedure.—The amount of the sample should be such as contains between 0.002 to 0.08 g. chromium. The finely powdered material is fused with ten times its weight of sodium peroxide in a nickel or iron crucible. (It appears unnecessary to heat to molten condition, provided the mass sinters.) After heating at dull red heat for ten minutes, the crucible is cooled and then upset in a 400-ml. beaker containing about 100 ml. of water. (The beaker should be immediately covered as the reaction is violent.) The crucible is washed out and removed, and the solution boiled to expel the peroxide. The solution is cooled and dilute sulfuric acid added until the alkali is neutralized and the solution is slightly acid. (Iron hydroxide dissolves, but manganese dioxide remains in suspension.) [15] If manganese is present, it is removed by filtration. To the filtrate 15 ml. of phosphoric-sulfuric acid mixture is now added and, from a burette, a measured excess of standard ferrous ammonium sulfate. (With an excess of ferrous salt the solution turns green.) Four drops (0.2 ml.) of diphenylamine indicator are now added and the excess of ferrous salt titrated with standard potassium dichromate. The green color changes to a blue green and then to an intense blue or violet color. (If the end-point is overrun,

[15] The ferric hydroxide occludes chromium; hence solution of the iron with acid and reprecipitation is necessary to recover chromium.

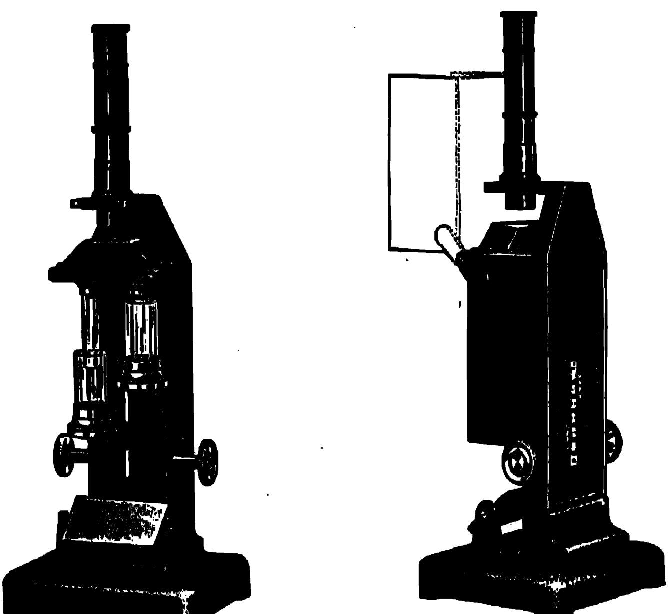
titrate back with ferrous sulfate to a green color and repeat the dichromate titration. Convert the reagents to exact equivalents, i.e., terms of 0.1 N solution.) The difference between the ml. of ferrous solution and the dichromate reagent multiplied by the chromium equivalent represents the chromium in the sample. One ml. 0.1 N solution is equivalent to 0.001734 g. chromium.

NOTES.—1. If it is desired to filter off the iron and manganese precipitates, it will be necessary to filter through asbestos or to neutralize the caustic with ammonium carbonate (1.5 times as much as peroxide used in fusion), boil and filter through paper.

2. If the iron precipitate has been dissolved and much manganese is present, the precipitate may be filtered off. Manganese dioxide does not occlude an appreciable amount of chromium.

3. Chrome steels may be dissolved with acid followed by treatment with permanganate to oxidize the iron.

4. It is evident that neither ferric salt nor dichromate alone produces the blue color, but an excess of dichromate in presence of ferric iron. If much chromium is present, the end-point may be overrun owing to the depth of color, the excess of dichromate causing a greenish-blue color to reappear. Back titration with ferrous sulfate will restore the blue or violet color, and an excess will change the color to blue-green.



By courtesy of Arthur H. Thomas Company, Philadelphia, Pa.

FIG. 38.—Colorimeter.

DIRECTIONS FOR THE USE OF A DUBOSCQ TYPE OF COLORIMETER

The mirror is turned so that the two halves of the field appear to be equally illuminated with the cups clean and empty. The solutions are then poured into the cups. The cup containing the standard solution is then lowered to a definite thickness of the standard solution between the bottom of the cup and the end of the plunger. With this movement the half of the field corresponding to the standard solution is seen to darken, while the other half remains luminous and colorless. If the cup containing the unknown solution is now moved in its turn, the two halves of the field are brought to the same intensity, after which the height at which the two liquid columns display this

equal absorptive power is read by means of this scale. The proportion of coloring matter in two solutions is inversely proportional to the heights of the two columns necessary to obtain the same intensity of illumination; thus if the standard tube is set at 10 mm., and the solution under examination is the same intensity of color at 20 mm., the latter is just one-half the concentration of the standard. This is usually expressed by the formula:

$$\frac{\textit{Color of test solution}}{\textit{Color of standard solution}}=\frac{\textit{Height of standard solution}}{\textit{Height of solution to be tested}}.$$

If, therefore, the scale reading is 20 mm. for the standard, and 15 mm. for the solution to be tested, the formula reads:

$$\frac{20}{15}=1.33.$$

If, for example, the standard solution contains 4 ml. of coloring matter in 100 ml., the solution under test will be found to contain $4\times1.33=5.32$ ml. in 100 ml.

ANALYSIS OF HIGH SPEED STEEL

DETERMINATION OF CHROMIUM AND VANADIUM

Two (2.000) grams of the sample are dissolved in 50 ml. of sulfuric acid (1 to 3) in a 400-ml. beaker at a temperature of approximately 50 to 60° C. Ten (10) ml. of " perhydrol " (30% H_2O_2) diluted with 20 ml. of water are added and the solution is heated to boiling for several minutes. The solution is then diluted to a volume of 100 ml. with hot water, filtered on an 11 cm. paper and the residue washed from 12 to 15 times with warm water. The filtrate (contained in a 600-ml. beaker) is evaporated almost to fumes of sulfur trioxide to insure the removal of the excess of " perhydrol," diluted with water to 100 ml., and reserved.

The tungstic acid precipitate and the paper on which it was filtered are transferred back to the original 400-ml. beaker. Twenty-five (25) ml. of hot water are added and the filter is beaten to a pulp by means of a glass stirring rod. Ten (10) grams of NH_4Cl and a *slight* excess of ammonium hydroxide (sp. gr. 0.90) are added and the solution is gently warmed for about 5 minutes. The liquid is filtered on an 11 cm. paper, the residue and filter paper washed from 18 to 20 times with 5% ammonium chloride solution, and ignited in porcelain at a dull red heat to burn off the carbon of the filter paper. The residue is brushed into a 30-ml. " Armco " iron crucible and fused with approximately 3 grams of Na_2O_2. The melt, when cool, is dissolved in 50 ml. of water, the solution acidified with sulfuric acid and added to the main solution obtained as described in the preceding paragraph.

To the warm solution (which should have a total volume of approximately 250 ml.) there are added from 8 to 10 ml. of a 0.5% solution of silver nitrate, from six to eight drops of strong potassium permanganate solution (25 grams per

liter), and a sufficient weight of ammonium persulfate salt (from 3 to 5 grams are required) to thoroughly oxidize the chromium, and the liquid is boiled for at least five minutes. The permanganate is consumed in the oxidation of the chromium but its color again appears as soon as the chromium has been completely oxidized by the ammonium persulfate. Its permanent reappearance is proof that all the chromium has been oxidized. Twenty (20) ml. of 10% sodium chloride solution are introduced and the solution is boiled until the permanganate or any manganese dioxide has completely disappeared. Should this take longer than 3 minutes' boiling, an additional 10 ml. of 10% sodium chloride are added and the boiling is continued. The solution is cooled to room temperature, treated with 3 ml. of phosphoric acid (syrup, sp. gr. 1.725), and an excess of from 5 to 10 ml. of 0.1 N ferrous ammonium sulfate solution is added from a 100-ml. burette. This will cause the reduction of the chromium to the trivalent state as shown by the following equation:

$$2H_2CrO_4+6FeSO_4+6H_2SO_4=Cr_2(SO_4)_3+3Fe_2(SO_4)_3+8H_2O.$$

The burette reading is noted and 0.1 N potassium permanganate is run in with vigorous stirring until the solution has assumed a faint pink color which remains permanent for at least 30 seconds.

The excess of ferrous sulfate used, is of course, oxidized to ferric sulfate. Therefore, subtraction of the number of ml. of 0.1 N permanganate used from the number of ml. of 0.1 N ferrous ammonium sulfate taken, gives the volume of 0.1 N ferrous ammonium sulfate required to reduce the chromic acid. One ml. of 0.1 N ferrous ammonium sulfate is equivalent to 0.001734 gram chromium.

Immediately after completing the titration of the chromium, the determination of the vanadium may be conducted in the following manner: The solution is titrated with an approximately 0.05 N solution of potassium permanganate (it is not necessary to determine the exact strength of this solution) with vigorous stirring, until a strong pink color has developed which remains permanent for 30 seconds. An approximately 0.05 N ferrous ammonium sulfate solution (it is unnecessary to determine the exact strength of this solution) is next run in with constant stirring until a drop of the solution, when added on a spot plate to a drop of a 0.1% solution of potassium ferricyanide, results in the *immediate* formation of a blue color, showing that an excess of ferrous iron has been added. An excess of 10 ml. of ferrous ammonium sulfate is then introduced and after the solution has been stirred for one minute, the excess of ferrous salt over that required to reduce the vanadium, is oxidized by adding 8 ml. of 15% ammonium persulfate and *vigorously stirring the liquid for one minute* longer. The ammonium persulfate oxidizes the excess of ferrous iron but does not affect the reduced vanadium. The reactions which take place are shown by the following equations:

$$2H_3VO_4+2FeSO_4+3H_2SO_4=V_2O_2(SO_4)_2+Fe_2(SO_4)_3+6H_2O,$$

$$\underset{\text{(excess)}}{2FeSO_4}+(NH_4)_2S_2O_8=Fe_2(SO_4)_3+(NH_4)_2SO_4.$$

An 0.05 N solution of potassium permanganate is then run into the solution with constant stirring until a faint pink color, *which remains permanent for 30*

seconds, has developed:

$$5V_2O_2(SO_4)_2+2KMnO_4+22H_2O=10H_3VO_4+K_2SO_4+2MnSO_4+7H_2SO_4.$$

The permanganate solution is standardized against pure sodium oxalate obtained from the Bureau of Standards. A " blank " is run by dissolving 2 grams of " American Ingot Iron " or iron drillings free from vanadium and chromium in 100 ml. of sulfuric acid (1 to 4) and 20 ml. of nitric acid (sp. gr. 1.20) and putting the solution through all of the operations of a regular analysis. If the cast iron or steel contains an appreciable amount of *chromium*, a weight of potassium bichromate containing the amount of chromium in the sample is dissolved in the acids with the ingot iron, or, a sample of steel containing approximately the same amount of chromium but free from vanadium may be used. Each ml. of 0.05 N potassium permanganate is equal to 0.002548 gram vanadium on a one gram sample.

Solutions Required. *Silver Nitrate Solution, 0.5%.*—Five (5) grams of silver nitrate are dissolved in 1000 ml. of distilled water.

Sodium Chloride, 10%.—One hundred (100) grams of salt are dissolved in 1000 ml. of distilled water.

Standard Ferrous Ammonium Sulfate Solution. (One ml. of 0.1 normal solution equals 0.001734 gram of chromium).—This solution is prepared by dissolving 39.25 grams of $FeSO_4\cdot(NH_4)_2SO_4, 6H_2O$ in 1 liter of distilled water containing 20 ml. of dilute sulfuric acid (1 : 1). The solution is mixed thoroughly and standardized against 0.1 normal potassium permanganate, which has in turn been standardized against Bureau of Standards' sodium oxalate. This solution should be standardized just before using, as its value may change from day to day.

Standard Potassium Permanganate Solution (0.1 normal).—This solution should contain 3.1606 grams per liter; it is prepared by dissolving 3.18 grams of the purest obtainable permanganate in 300 ml. of boiling water, cooling to room temperature, filtering on acid washed and ignited asbestos and making up to 1 liter and mixing thoroughly. After a preliminary standardization against sodium oxalate (obtained from the Bureau of Standards), the solution is diluted so as to be exactly 0.1 normal and the strength verified by a second comparison with sodium oxalate. This solution should be kept in a dark bottle.

DETERMINATION OF CHROMIUM IN A SOLUBLE CHROMATE

To a concentrated solution of potassium iodide is added a known amount of the soluble chromate dissolved in a little water. The liberated iodine is now titrated with standard thiosulfate reagent.

One ml. of N/10 $Na_2S_2O_3=0.001734$ g. Cr.

DETERMINATION OF CHROMIUM IN CHROMITE

About 0.2 g. of the powdered ore is fused with ten times its weight of Na_2O_2 in a porcelain crucible, placed inside a larger crucible. The melt is dissolved in water and the $Fe(OH)_3$ filtered off. The filtrate is evaporated to

dryness, the residue taken up with as little water as possible and about two grams of KI added. The solution is now diluted to about 300 ml. and the liberated iodine titrated with standard thiosulfate.

One ml. of N/10 $Na_2S_2O_3$ = 0.001734 g. Cr.

Oxidations of Chromium.—Small amounts of chromium may be oxidized by fusion with Na_2CO_3 and KNO_3, large amounts by fusion with Na_2O_2.

In acid solution oxidation is effected by PbO_2 or $KClO_3$ or $K_2S_2O_7$ or $(NH_4)_2S_2O_7$ (in presence of $AgNO_3$). Perchloric acid is useful in oxidation.[16] Potassium bromate may be used.[17]

ANALYSIS OF CHROME ORES[18]

The exact analysis of chrome ore is a matter of some difficulty, involving the separation and determination of large amounts of chromium, iron, aluminum, and magnesium. Although chromite is one of the most stable of the common minerals, complete decomposition may be obtained by heating the ore with perchloric and sulfuric acids or by fusion with sodium peroxide or a mixture of sodium carbonate and borax. The methods here described for the determination of chromium, iron, silica, alumina, lime, and magnesia offer the advantages of exceptional accuracy and simplicity of manipulation.

DETERMINATION OF CHROMIUM

Chromium can be determined more quickly and more accurately on a separate portion of the sample than on the same portion used for determining the other constituents. One (1.0000) gram of the 100-mesh ore, which has been dried for 2 hours at 105–110° C., is weighed, preferably from a weighing bottle, transferred to a 30-ml. Armco iron crucible, and fused over a gas flame with about 8 grams of dry sodium peroxide. The fusion should be made by revolving the crucible around the outer edge of the flame of a laboratory burner until the contents have melted down quietly; the temperature is then increased to a medium red heat for 3 to 5 minutes and a rotary motion is given to the fused material to prevent spraying. Suitable iron crucibles, containing only a trace of chromium, can be obtained from the Consolidated Manufacturing

[16] J. J. Lichtin, Ind. Eng. Chem., Anal. Ed. 2, 126, 1900.

[17] Kolthoff and Sandell, Ind. Eng. Chem., Anal. Ed. 2, 140, 1930.

[18] Thomas R. Cunningham and Thomas R. McNeill. Union Carbide & Carbon Research Laboratories, Inc., Long Island City, N. Y., and Electro Metallurgical Company, Niagara Falls, N. Y. Ind. Eng. Chem., Anal. Ed. 1, 70, 1929.

Company, Dayton, Ohio. Ordinary iron crucibles, which may contain significant amounts of chromium, should be avoided.

When the crucible has partly cooled, and while tightly covered, it is tapped on an iron plate to loosen the fusion in a solid cake. This is transferred to a 600-ml. covered beaker and treated with 200 ml. of warm water. The crucible is also rinsed with water. The solution is treated with 60 ml. of sulfuric acid (1 : 1) and 5 ml. of nitric acid (sp. gr. 1.42) and is then boiled for several minutes until all iron scale from the crucible has dissolved. From 20 to 25 ml. of a 0.5% solution of silver nitrate, 1 or 2 drops of strong potassium permanganate (25 grams per liter) and 3 to 5 grams of ammonium persulfate (to oxidize the chromium completely) are added and the liquid is then boiled for 5 minutes. Twenty milliliters of a 10% solution of sodium chloride are introduced and the solution is boiled for 5 to 10 minutes after the permanganate or any manganese dioxide has completely disappeared, to make sure that all chlorine has been expelled. The solution is cooled to room temperature, treated with 3 ml. of phosphoric acid (syrup, sp. gr. 1.725), and an excess of 5 ml. of 0.1 N ferrous ammonium sulfate solution is added from a 100-ml. burette. This will cause the reduction of the chromium to the trivalent state, as shown by the following equation:

$$2H_2CrO_4+6FeSO_4+6H_2SO_4=Cr_2(SO_4)_3+3Fe_2(SO_4)_3+8H_2O.$$

The burette reading is noted and 0.1 N potassium permanganate solution is run in with vigorous stirring to the first faint permanent darkening of the clear green color.

The excess of ferrous ammonium sulfate naturally is oxidized to ferric sulfate; wherefore, subtraction of the volume of 0.1 N potassium permanganate used from the volume of 0.1 N ferrous ammonium sulfate taken gives the volume of 0.1 N ferrous ammonium sulfate required to reduce the chromic acid. The ferrous ammonium sulfate solution is prepared by dissolving 39.2 grams of the salt in 1 liter of water (1 ml. = 0.001734 gram chromium) and it is standardized against 0.1 N potassium permanganate; this standardization must be made every day the solution is used, as this gradually grows weaker as a result of oxidation. The 0.1 N potassium permanganate is standardized against sodium oxalate obtained from the Bureau of Standards.[19]

DETERMINATION OF IRON AND ALUMINA

One-half (0.5000) gram of the sample, which has been ground to an impalpable powder in an agate mortar and dried for 2 hours at 105–110° C., is weighed preferably from a weighing bottle, and treated in a 300-ml. covered casserole with 50 ml. of sulfuric acid (1 : 4) and 5 ml. of perchloric acid (sp. gr. 1.54). The liquid is heated gently until fumes of sulfur trioxide are freely evolved. This treatment should result in a complete decomposition of the ore except some chrome ores which contain quartz.

An alternate method of decomposition is to fuse a 0.5000-gram sample of the dry agate-ground ore with a mixture of 5 grams of sodium carbonate and 2 grams of powdered fused borax ($Na_2B_4O_7$) in a covered 50-ml. platinum crucible.

[19] Fowler and Bright, J. Res. Natl. Bur. of Stands. 15, 493 (1935).

The fusion must be maintained at a temperature of approximately 1100° C. for 20 minutes, while a rotary motion is given to the crucible from time to time to stir up any unattacked particles of ore on the sides or bottom. When cool, the melt is dissolved in 50 ml. of hydrochloric acid (1 : 4) contained in a 300-ml. covered casserole. The solution is evaporated on a steam bath almost to dryness, 50 ml. of methanol and 20 ml. of hydrochloric acid (sp. gr. 1.19) are added and the evaporation is continued just to dryness. The residue is moistened with 10 ml. of nitric acid (sp. gr. 1.42) and heated for 5 minutes to decompose any remaining alcohol. Twenty-five (25) ml. of perchloric acid (60%) are introduced and the solution is heated cautiously until fumes of perchloric acid begin to be evolved, and the fuming continued for at least 10 minutes longer to insure the complete oxidation of the chromium to chromic acid.

The solution is cooled rapidly, about 50 ml. of water added, boiled for several minutes to expel free chlorine and cooled to room temperature. The solution is filtered on an 11-cm. paper containing a small amount of ashless paper pulp and the silica washed thoroughly with cold water, ignited in platinum, first at a dull red heat until the carbon has burned and finally at 1100° C. for 10 minutes. The crucible and silica are cooled in a desiccator, weighed and treated with 1 drop of sulfuric acid and 1 to 2 ml. of hydrofluoric acid (48%) and the solution is evaporated to dryness. The crucible is again ignited for a few minutes at 1100° C., cooled and weighed. The loss in weight, multiplied by 200, gives the percentage of SiO_2 in the sample. The small residue which usually remains is fused with about 0.5 gram of sodium pyrosulfate, dissolved in a few ml. of hot water, and added to the filtrate from the silica. The solution collected in a 250-ml. beaker is boiled down to a volume of about 100 ml. A slight excess of a 6.5% solution of lead nitrate is added with vigorous stirring to precipitate the chromium (1 ml. of this solution will precipitate 10 mg. of chromium) and the solution is filtered on a 9-cm. paper containing some ashless paper pulp. The paper and precipitate are washed at least 15 times with hot water and discarded. The filtrate and washings, which should have a volume of 175 to 200 ml., are collected in a 250-ml. beaker.

The solution is treated with a brisk stream of hydrogen sulfide for about 10 minutes, filtered on a 9-cm. paper into a 400-ml. beaker and the lead sulfide, together with any platinum from the crucible, or other metals of the second group, are washed well with hydrogen sulfide water containing 1% sulfuric acid, and discarded.

The filtrate is boiled to expel hydrogen sulfide, treated with 1 ml. of nitric acid (sp. gr. 1.42) and the boiling continued for several minutes to oxidize the iron to the ferric state. Five grams of ammonium chloride and a considerable quantity of ashless paper pulp are introduced and the solution is rendered very faintly ammoniacal by the addition of dilute, filtered ammonium hydroxide (1 to 4). The solution is heated to boiling for 1 or 2 minutes (no longer), the precipitate is allowed to settle, and is then filtered and washed 10 or 12 times with a hot 2% solution of ammonium chloride. The precipitate is rinsed from the filter back into the beaker with a jet of warm water and dissolved in 50 ml. of hydrochloric acid (1 to 4). A second ammonia separation is made in a similar manner, the precipitate being filtered on the same paper. The two filtrates are combined and reserved for the determination of lime and magnesia.

The hydroxide precipitate is dissolved in 60 ml. of hot hydrochloric acid (1 to 4) and the solution diluted with cold water to a volume of 100 ml. Some ashless paper pulp is added, the liquid is cooled to about 20° C. and the iron and titanium are precipitated by the addition (drop-wise and with constant stirring) of a cold, freshly prepared, filtered 6% solution of cupferron (ammonium nitrosophenylhydroxylamine, $C_6H_5N \cdot NO \cdot ONH_4$) in slight excess. An excess is known to be present when a drop of the precipitant forms a white precipitate which quickly goes into solution. The precipitate is filtered on an 11-cm. paper with the aid of gentle suction, washed thoroughly with cold 10% hydrochloric acid and ignited at a low temperature in a porcelain or silica crucible. The resulting oxides are treated in a 150-ml. beaker with 10 ml. of hydrochloric acid (sp. gr. 1.19) and heated until the iron oxide has all dissolved. Iron is determined in this solution by the Zimmermann-Reinhardt method. If the determination of titanium is desired, the ignited oxides are fused with potassium pyrosulfate, the melt dissolved in sulfuric acid (1 to 4) and the titanium determined colorimetrically. The iron is then determined in this solution by one of the approved methods.

The filtrate from the cupferron precipitate, which contains all of the aluminum, is concentrated to a volume of 40 to 50 ml. Fifty ml. of nitric acid (sp. gr. 1.42) are added and the evaporation is continued slowly until the volume has again been reduced to 60 to 75 ml. Ten ml. of perchloric acid (60%) are added and the solution is evaporated until fumes of perchloric acid begin to be evolved and the fuming continued for at least 5 minutes, to insure the complete destruction of the cupferron. The perchloric acid residue is taken up in 50 ml. of water, boiled for several minutes, and filtered to remove any silica. Five grams of ammonium chloride and some ashless paper pulp are introduced and the aluminum is precipitated by the addition of ammonium hydroxide (1 to 4) in very faint excess. The liquid is boiled for 1 or 2 minutes (no longer), the precipitate filtered and washed 18 or 20 times with 2% ammonium chloride solution, ignited in a weighed covered platinum crucible, first at a low heat and finally to constant weight at 1100 to 1150° C., cooled, and weighed. The increase in weight represents the amount of Al_2O_3 present in the ore, and only a small proportion of the P_2O_5.

The phosphorus content of the chrome ores usually encountered is so low that the error introduced by its inclusion with the alumina is negligible, except when the highest accuracy is desired. To make correction for phosphorus, the oxides are fused with 6 to 8 grams of sodium carbonate, and the fusion is dissolved in water and made acid with an excess of about 2 ml. of nitric acid. Phosphorus is determined in this solution by any one of the approved methods.

DETERMINATION OF LIME AND MAGNESIA

The combined ammoniacal filtrates from the iron and aluminum hydroxide precipitates are made slightly acid with hydrochloric acid, evaporated to a volume of approximately 150 ml., and cooled to 15° C. Twenty milliliters of a 10% solution of diammonium phosphate are added and ammonium hydroxide (sp. gr. 0.90) is then slowly introduced, drop by drop, with vigorous stirring until the solution is ammoniacal and a crystalline precipitate appears. Fifteen milliliters of ammonia (sp. gr. 0.90) are added, the liquid is stirred thoroughly

and finally chilled by surrounding the beaker with crushed ice. After standing for several hours with frequent stirring, or preferably overnight if allowed to stand at room temperature, the solution is filtered on a 9-cm. blue ribbon paper, and the precipitate is washed three or four times by decantation with cold 2.5% ammonia water. Twenty-five milliliters of hydrochloric acid (1 : 1) are poured through the filter, the filtrate being collected in the original beaker containing the bulk of the precipitate, and the filter is washed thoroughly with 5% hydrochloric acid. The solution is diluted with cold water to a volume of 150 ml., 3 ml. of a 10% solution of diammonium phosphate are added, and the precipitation is repeated as previously described. The precipitate is allowed to stand for 2 hours surrounded by crushed ice, filtered, washed ten or twelve times with cold 2.5% ammonia water, and ignited in a weighed platinum crucible, first at a dull red heat until the carbon has been burned, and finally to constant weight at 1000–1050° C.

The pyrophosphate precipitate thus obtained—which will contain all the lime, magnesia, any manganese present, and small amounts of silica—is dissolved in 20 ml. of hot dilute (1 : 4) hydrochloric acid, the solution is filtered on a 7-cm. paper to remove silica, and the filter is washed well with hot water. The paper and silica are ignited and the silica determination is completed in the usual manner. The weight of silica found is deducted from the weight of the magnesium pyrophosphate obtained as previously described.

Ten milliliters of sulfuric acid (1 : 1) are added to the filtrate from the silica and the solution is evaporated to fumes of sulfur trioxide. Five milliliters of water and enough absolute alcohol to constitute 90 to 95% of the total volume are added, and the solution is stirred vigorously for several minutes. After the calcium sulfate precipitate has settled for 2 or 3 hours, preferably overnight, it is filtered on a 9-cm. blue ribbon paper and the paper and precipitate are washed free from phosphoric acid with 80% alcohol. The calcium sulfate is dissolved in 25 ml. of hot 10% hydrochloric acid and the solution is heated to boiling. One-tenth gram of oxalic acid is added and the lime is precipitated by the slow addition, with vigorous stirring, of dilute ammonia (1 : 3) in slight excess, the determination being completed in the usual manner. The weight of calcium oxide found is calculated to tricalcium phosphate ($Ca_3(PO_4)_2$) by multiplication by 1.8443, and this amount is deducted from the weight of the magnesium pyrophosphate obtained as previously described.

The alcoholic filtrate from the calcium sulfate is evaporated until strong fumes of sulfur trioxide are evolved and all organic matter is destroyed. After the solution has cooled, the residue is dissolved in 25 ml. of nitric acid (sp. gr. 1.135) and finished for manganese by the bismuthate method. Any manganese found is calculated to manganese pyrophosphate ($Mn_2P_2O_7$), (factor, 2.5842), and this is deducted from the weight of magnesium pyrophosphate. The weight of $Mg_2P_2O_7$ is multiplied by 0.3621 and by 200 to obtain the percentage of MgO in the sample.

ANALYSIS OF CHROME-IRON AND CHROME-IRON-NICKEL ALLOYS

DETERMINATION OF CHROMIUM

PERSULFATE METHOD

One (1.0000) gram of the alloy is treated with 50 ml. of sulfuric acid (1 to 4) in a 600-ml. covered beaker at a temperature of from 50 to 60° C. When practically all action has ceased, 0.5 ml. of hydrofluoric acid (48%) and 5 ml. of nitric acid (sp. gr. 1.42) are introduced and the solution is boiled for several minutes to expel oxides of nitrogen. If an insoluble residue should remain, the solution should be diluted with 50 ml. of hot water, filtered on a 9-cm. paper and the paper and residue washed thoroughly with hot water. The filtrate is reserved.

The residue is ignited at a dull red heat and fused in platinum with several grams of sodium carbonate, or in an "Armco" iron crucible with several grams of dry sodium peroxide. The iron crucibles (practically free from Cr) may be purchased from The Consolidated Manufacturing Company, Dayton, Ohio. The melt, when cool, is dissolved in 50 ml. of hot water, acidified with sulfuric acid (1 to 4), and added to the main solution.

To the warm solution (which should have a total volume of approximately 250 ml.) there are added from 15 to 25 ml. of a 0.5% solution of silver nitrate, from six to eight drops of strong potassium permanganate (25 grams per liter), and a sufficient weight of ammonium persulfate salt (from 8 to 10 grams are required) to thoroughly oxidize the chromium, and the liquid is boiled for at least five minutes. The permanganate is consumed in the oxidation of the chromium but its color again appears as soon as the chromium has been completely oxidized by the ammonium persulfate. Its permanent reappearance is proof that all the chromium has been oxidized. Twenty (20) ml. of 10% sodium chloride solution are introduced and the solution is boiled until the permanganate or any manganese dioxide has completely disappeared. Should this take longer than 3 minutes' boiling, an additional 10 ml. of 10% sodium chloride are added and the boiling is continued. The solution is cooled to room temperature, treated with 3 ml. of phosphoric acid (syrup, sp. gr. 1.725), and an excess of from 5 to 10 ml. of 0.1 N ferrous ammonium sulfate solution is added from a 100-ml. burette. This will cause the reduction of the chromium to the trivalent state as shown by the following equation:

$$2H_2CrO_4+6FeSO_4+6H_2SO_4=Cr_2(SO_4)_3+3Fe_2(SO_4)_3+8H_2O.$$

The burette reading is noted and 0.1 N potassium permanganate is run in with vigorous stirring until the solution has assumed a faint pink color which remains permanent for at least 30 seconds.

The excess of ferrous sulfate used, is of course, oxidized to ferric sulfate. Therefore, subtraction of the number of ml. of 0.1 N permanganate used from the number of ml. of 0.1 N ferrous ammonium sulfate taken, gives the volume of 0.1 N ferrous ammonium sulfate required to reduce the chromic acid. One ml. of 0.1 N ferrous ammonium sulfate is equivalent to 0.001734 gram chromium.

In the case of Cr steel from 3 to 5 grams are dissolved in 75 ml. of H_2SO_4 (1 to 4). Ten ml. of HNO_3 is added to oxidize the ion. Any residue is worked as described in the 2d paragraph. Ten ml. of 0.5% solution of $AgNO_3$ will be

sufficient for 5 grams of a 1% Cr steel and only 2 to 3 grams of ammonium persulfate will be needed.

Solutions Required.—These are the same as are described in the preceding section, "Analysis of High Speed Steel."

ANALYSIS OF FERROCHROMIUM AND CHROMIUM METAL[20]

DETERMINATION OF CHROMIUM

One-half (0.5000) gram of the sample of ferrochromium or 0.4000 gram of chromium metal is transferred to a 30-ml. "Armco" iron crucible. Samples of low carbon ferrochromium are crushed to pass through a 40-mesh screen, while high carbon ferrochromium and chromium metal are reduced to 100-mesh. The iron crucibles used may be purchased from the Consolidated Manufacturing Company, Dayton, Ohio. This iron contains approximately 99.89% metallic iron and only about 0.01% manganese and a trace of chromium. Approximately 8 grams of dry sodium peroxide are added and the contents of the crucible are mixed thoroughly and fused carefully in an electric muffle furnace heated to from 700 to 800° C. A gas flame may be used instead of a muffle furnace. This is done by revolving the crucible around the outer edge of the flame of a laboratory burner until the contents have melted down quietly, when the temperature is increased to a medium red heat and a rotary motion is imparted to the fused material to prevent spattering and to stir up any unattacked particles of alloy on the bottom or sides. If these directions are followed carefully a very quiet fusion with complete decomposition of the alloy will result.

When the crucible has partly cooled, and while tightly covered, it is tapped on an iron plate several times to loosen the fusion in a solid cake. The cake is transferred to a 600-ml. covered beaker and treated with 200 ml. of warm water. The reaction between the water and the excess of sodium peroxide is quite violent so that care should be exercised to avoid loss by spattering. The crucible is rinsed with a jet of water, approximately ½ gram of sodium peroxide introduced and the solution is boiled briskly for at least 5 minutes to insure complete oxidation of the chromium to the hexavalent state and to decompose completely the excess of sodium peroxide.

By the fusion, the chromium, silicon, carbon, phosphorus and sulfur are completely converted to sodium chromate, silicate, carbonate, phosphate and sulfate, respectively, and the iron and manganese to ferric oxide and manganese peroxide, respectively. The excess of sodium peroxide is decomposed by the boiling water, sodium hydroxide being formed and oxygen liberated. It is essential that the excess of sodium peroxide be destroyed completely, otherwise

[20] Electro Metallurgical Company.

when the solution is subsequently acidified hydrogen peroxide will form and cause low results.

Two hundred (200) ml. of boiling water are added and the precipitate is allowed to settle and the strongly alkaline solution is filtered on a pad of ignited asbestos, *gentle suction* being employed. An asbestos rather than a paper filter must be employed, as paper exerts a noticeable reducing action on strong chromate solutions. The precipitate is transferred to the filter and washed thoroughly with hot water to remove all sodium chromate. After having transferred the residue of iron oxide, etc., to the filter, at no time should the filter be allowed to suck dry until the washing is considered to be complete, or else chromium will be retained by the residue.

The filtrate from the iron oxide, manganese peroxide, etc., is cooled, acidified by addition of 50 ml. of sulfuric acid (1 to 1), again cooled to room temperature, transferred to an 800-ml. battery jar and there are added 3 ml. of phosphoric acid (sp. gr. 1.725) and a sufficient amount of cold distilled water to bring the volume to 500 ml. (as shown by a mark on the jar), when it is ready for titration.

The only object of the filtration is to remove the small amount of manganese present which under the prevailing conditions forms the hydrated peroxide and would cause high results by reacting with ferrous ammonium sulfate in the subsequent titration.

$$MnO_2+2FeSO_4+2H_2SO_4=MnSO_4+Fe_2(SO_4)_3+2H_2O.$$

If desired the determination may be made by the persulfate method, which is as follows: One-half (0.5000) gram of the alloy is fused as described above in paragraph 1. When the crucible has partly cooled, and while tightly covered, it is tapped on an iron plate several times to loosen the fusion in a solid cake. The cake is transferred to a 600-ml. covered beaker and treated with 150 ml. of warm water. The crucible is rinsed with water and the solution is treated with 60 ml. of sulfuric acid (1 to 1) and 5 ml. of nitric acid (sp. gr. 1.42) and boiled for several minutes until all iron scale from the crucible has dissolved. From 20 to 25 ml. of a 0.5% solution of silver nitrate, 2 to 4 drops of strong potassium permanganate (25 grams per liter) and 3 to 5 grams of ammonium persulfate (to oxidize the chromium completely) are added and the liquid is boiled for 5 minutes. Twenty (20) ml. of a 10% solution of sodium chloride are introduced and the solution is boiled for 10 minutes after the permanganate or any manganese dioxide has completely disappeared, in order to make sure that all chlorine has been expelled. The solution is cooled to room temperature, transferred to an 800-ml. battery jar and there are added 3 ml. of phosphoric acid (sp. gr. 1.725) and a sufficient amount of cold distilled water to bring the volume to 500 ml.

The chromium in the solution obtained by one of the previously described methods is determined by titration with ferrous ammonium sulfate and potassium permanganate in the following manner:

From a pipette (an automatic pipette is convenient when many determinations have to be made) 175 ml. of standard, approximately 0.1 N ferrous ammonium sulfate are run into the solution with stirring. This amount is nearly sufficient to reduce all of the chromium in a one-half gram sample of 70% alloy from the sexivalent to the trivalent condition. The small additional

amount necessary is measured from a burette, several ml. excess being used. The point where reduction is complete can be told by the deep pure green color developed, or by testing a drop of the liquid with a drop of dilute potassium ferricyanide solution, which gives a blue color with any excess of ferrous iron present.

The equation representing the reaction that occurs upon addition of the ferrous ammonium sulfate may be expressed as follows:

$$Na_2Cr_2O_7+6FeSO_4+7H_2SO_4=Cr_2(SO_4)_3+3Fe_2(SO_4)_3+Na_2SO_4+7H_2O.$$

To secure good light the battery jar is elevated by means of two porcelain boats about one-half an inch above a white tile, and the excess of ferrous ammonium sulfate is determined by titration with standard 0.1 N potassium permanganate. The first faint permanent darkening of the clear green color is taken as the end-point. Addition of more permanganate increases the depth of the color, which finally becomes purple. The end-point is quite sharp and well defined, but requires some practice.

The number of ml. of 0.1 N permanganate solution used to titrate back with is deducted from the number of ml. of 0.1 N ferrous ammonium sulfate solution taken (obtained by multiplying the number of ml. of the approximately 0.1 N solution by the normality factor), the remainder being the amount of 0.1 N ferrous ammonium sulfate solution actually required to reduce the chromium, each ml. of which is equal to 0.001734 gram of chromium. The number of ml. multiplied by 17.34, multiplied by 2, gives the percentage of chromium in the sample.

None of the elements ordinarily found in ferrochromium interfere with this method.

PREPARATION AND STANDARDIZATION OF SOLUTIONS

Standard Ferrous Ammonium Sulfate, Approximately 0.1 N

The preparation and standardization are described in a previous section "Analysis of High Speed Steels," page 295. The solution keeps much better if it is blown with a stream of carbon dioxide from a cylinder.

It is preferable to standardize against dichromate, which gives the same result as the permanganate and oxalate method. Recrystallize twice the purest potassium dichromate, dry at 150° C., grind it to a fine powder and dry further at 150° to constant weight and preserve the product in a glass stoppered bottle. One (1.000) gram of this dichromate, which contains approximately the same amount of chromium as a 0.5000 gram sample of 70% ferrochrome, is dissolved in cold water, acidified with 20 ml. of sulfuric acid (1 to 1) and 3 ml. of phosphoric acid (sp. gr. 1.725), diluted with cold water to 500 ml. and titrated with the ferrous ammonium sulfate solution and permanganate exactly as described above for a regular analysis.

Standard Potassium Permanganate Solution (0.1 Normal).—The preparation and standardization are described in a preceding section "Analysis of High Speed Steels," page 295.

We are indebted to Thos. R. Cunningham for the sections on ferrochrome, chromium metal, the analysis of high-speed steels and the analysis of chromium ores.

COBALT[1]

Co. *at.wt.* 58.94; *sp.gr.* 8.7918; *m.p.* 1480° C.; *b.p.* 2900° C.; *oxides* Co_3O_4, Co_2O_3, CoO, CoO_2.

The term cobalt, which comes from the German Kobald, meaning goblin, was applied during the period of Paracelsus and Agricola to substances resembling metallic ores, but giving no metals on smelting. Later it was applied to a mineral that produced a blue color in glass. Impure cobalt was prepared by Brandt in 1735.

Cobalt is used in plating and as a constituent of ferrous and non-ferrous alloys and special steels. Its principal function in such is to impart added strength; heat, abrasion and corrosion resistance; and magnetic properties.

Cobalt in the form of its oxides finds use in ceramics as smalt, a cobalt potassium silicate. In conjunction with alumina, etc., the oxides are efficient catalysts for oxidation of ammonia to nitric acid. They are also used in the manufacture of cobalt chemicals, paints, enamels and driers.

Cobalt is generally associated with nickel, though it is less abundant. It occurs in sulfides, arsenides, arsenates, oxides, carbonates and silicates. The element is found in the form of metal in meteoric iron. The more commonly known minerals are linnaeite, Co_3S_4 or $(CoNi)_3S_4$; smaltite, $CoAs_2$ or $(CoNi)As_2$; cobaltite, CoAsS.

DETECTION

The ore or other substance to be examined is taken into solution by one of the methods outlined under Preparation and Solution of the Sample. The elements of the second group are removed by passing hydrogen sulfide gas and filtering. The hydrogen sulfide is boiled out of the filtrate and the iron oxidized with nitric acid. As ammonium salts are necessary to hold cobalt in solution, a few grams of either the chloride or the sulfate should be added, unless there is enough free acid in the solution to insure their presence after neutralization. Ammonium hydroxide in slight excess is added to precipitate iron, aluminum and chromium, and the precipitate, after boiling, is removed by filtration. If it is at all bulky it should be redissolved in acid and reprecipitated, as the

[1] Based on the chapter in the 4th edition; revised and largely rewritten by William L. Rigg, Chief Chemist, and Herbert C. Barlow, Research Chemist, Deloro Smelting and Refining Co., Ltd., Deloro, Ont.

hydroxides have a tendency to occlude cobalt. Unless this is done, cobalt may be overlooked in a sample containing only a trace. If cobalt is present in any considerable quantity, the filtrate will be pink, but this color may be masked by the presence of nickel.

The following confirmatory tests may now be made on the solution.

A. Phenyl-thio-hydantoic Acid.—A few ml. of the solution are slowly evaporated with a pinch of the salt, in a porcelain crucible lid. A pink or reddish coloration shows cobalt. The test is very sensitive.

B. Ammonium Sulfide.—A large portion of the ammoniacal solution is treated with hydrogen sulfide gas. This precipitates cobalt, nickel, manganese and zinc. The precipitation is seldom complete, owing to the formation of polysulfides, caused by the presence of oxidizing agents; a little ammonium sulfite helps to correct this. After collecting the precipitate, it is washed thoroughly with cold hydrochloric acid (sp.gr. 1.035), to remove manganese and zinc. A small quantity is then fused with borax in a loop of platinum wire. A blue color in the cold bead indicates cobalt.

The test is masked by large quantities of nickel, in which case the nitroso-beta-naphthol test may be made.

C. Nitroso-beta-naphthol.[2]—This reagent precipitates brick red cobalti-nitroso-beta-naphthol which is insoluble in dilute mineral acids. The solution of the salt must be freshly prepared each day and is made by dissolving 10 grams in 100 ml. of hot 50% acetic acid. To apply the test, the sulfides from the ammonium sulfide test are ignited to oxides in a porcelain crucible and dissolved in hydrochloric acid. After expelling most of the acid, the chlorides are diluted and the hot nitroso-beta-naphthol solution added till no further precipitation takes place. The precipitate may be filtered and after igniting to oxide, used for other confirmatory tests. It is claimed that the nitroso-beta-naphthol test will precipitate 0.01 mg. of cobalt. It may be used quantitatively.

This test may also be applied to the ammoniacal filtrate after acidifying with hydrochloric acid.

D. Potassium Nitrite.—This salt added to a solution which is slightly acid with acetic, precipitates cobalt as a yellow complex nitrite having the formula $2K_3Co(NO_2)_6 \cdot 3H_2O$.

The test may be conveniently applied to a hydrochloric acid solution of the oxides, obtained by igniting either the nitroso-beta-naphthol precipitate or the precipitate from the ammonium sulfide test. The free acid is neutralized with potassium hydroxide and the solution reacidified with acetic acid. The addition of a hot concentrated solution of potassium nitrite which has been slightly acidified with acetic acid, will precipitate the yellow potassium cobalti-nitrite, on standing.

The test is not applicable in the presence of ammonium salts.

E. Ammonium Thiocyanate.—A concentrated solution of ammonium thiocyanate added to a cobaltous solution, colors it blue. On dilution it becomes pink. Amyl alcohol, a mixture of amyl alcohol and ether, acetone or ethyl acetate, added to the solution and shaken, extracts this blue compound. The presence of free ammonia inhibits the reaction and must be neutralized with acetic acid. Iron thiocyanate, $Fe(CNS)_3$, colors the extract red and masks the blue of the cobalt. The addition of a concentrated solution of sodium car-

[2] Ilinski and V. Knorre, Ber., 18, 699 (1885).

bonate in slight excess precipitates ferric hydroxide and permits the blue to show. Two or 3 ml. concentrated ammonium acetate and 2 or 3 drops tartaric acid added to the solution will remove the color of the iron.[3] The masking effect of the iron may also be counteracted by the addition of a few drops stannous chloride. An excess of the chloride, however, tends to bleach out the color of the cobalt.[4]

F. Dicyandiamidine Sulfate.—A concentrated solution of dicyandiamidine sulfate and sodium hydroxide added to a cobalt solution to which ammonia has been added until the odor is distinctly descernible, and containing from 10 to 20 ml. of 10% sugar solution, will change the color of the solution to red or reddish violet. If large quantities of nickel are present, the color will be yellow or reddish yellow, after which the nickel compound will separate out in brilliant crystals, leaving the cobalt in solution, coloring it as described above.

The salt has been suggested as a substitute for dimethyl-glyoxime, in the separation of cobalt and nickel, but it offers no advantages.

ESTIMATION

Cobalt is usually estimated as metal; either reduced by hydrogen from the ignited oxide or reduced by electrolysis from an ammoniacal solution of its salts. Sometimes, however, it is estimated as oxide; usually Co_3O_4. The reduction of the oxide by hydrogen may be carried out in conjunction with any process giving an oxide, hydroxide, carbonate, nitrate, chloride or an organic compound, as a final product.

The reduction of the metal, in solution, by electrolysis, must be accomplished in a strongly ammoniacal solution, free from copper and nickel, as these metals are deposited with the cobalt on the cathode. When desirable the copper and nickel may be estimated after the electrolysis by dissolving the deposit from the cathode and proceeding in the usual manner.

PREPARATION AND SOLUTION OF THE SAMPLE

General Procedure for Ores.—The ores containing cobalt vary so widely in their chemical nature that it is difficult to lay down a method for treating all ores. However, as the principal ores contain the cobalt as a sulfide or arsenide the same general methods may be used in the majority of cases. In all cases it is necessary to prepare the sample for treatment by grinding finely. Usually either of the above ores may be brought into solution by heating with concen-

[3] Treadwell, Z. anal. Chem., 26, 105 (1901).
[4] R. V. Vorontzov, J. Appl. Chem. (U. S. S. R.), 8, 555 (1935).

trated nitric acid or a mixture of nitric and hydrochloric acids, except silver-bearing ores, which may usually be dissolved in a mixture of nitric acid and sulfuric acids.

While it is desirable to use no more acid than is necessary to bring the sample into solution, an excess will not interfere, as it may be driven off by evaporation and in the event of determining cobalt electrolytically it is essential that the solution be free from nitric acid, so that this evaporation becomes part of the procedure.

In the case of refractory ores which fail to decompose on attacking with nitric, hydrochloric or sulfuric acids, the insoluble matter is filtered off, washed, and treated with ammonium acetate to remove any lead sulfate which may be present. If the refractory character of the ore is known beforehand, the attack may begin with a preliminary nitric acid treatment to remove substances which are likely to attack platinum, and after filtering off the insoluble, washing it with ammonium acetate solution to remove lead, in case any galena has been oxidized to sulfate by the nitric acid. The ignited insoluble, from whichever method used, is then fused with either potassium bisulfate or a mixture of sodium and potassium carbonates, in a platinum crucible. On completion of the fusion, the melt is poured into a platinum basin, floating in a casserole filled with water. The melt chills into a button instantly. The crucible is washed out with hot water and hydrochloric acid and the washings, together with the button, are added to the main nitric acid filtrate. It is then proceeded with in the usual way, as outlined under Determination of Cobalt in Ores by Electrolysis.

When large quantities of ore have been taken for assay, the insoluble may be too large for the fusion procedure, in which case, it may be treated in a platinum basin with hydrofluoric acid and a little sulfuric acid till the silica has been eliminated; after which it is fumed, diluted and added to the main acid solution.

Cobalt Oxides.—As a general rule both Gray and Black Cobalt Oxides are readily soluble in hydrochloric acid (sp.gr. 1.2), unless they are very impure; in which case boiling with concentrated sulfuric acid or fusion with potassium bisulfate may be resorted to.

Metallic Cobalt, Nickel and Cobalt Alloys.—Metallic Cobalt dissolves readily in nitric acid, as do nickel and the ordinary cobalt alloys. There are, however, certain alloys of cobalt which require a fusion with sodium peroxide before they become amenable to treatment; others may be decomposed by the use of perchloric acid. Among the latter are cobalt, chromium, tungsten alloys, such as "Stellite"; the Method of Analysis for which is given under Special Procedures.

SEPARATIONS

SEPARATION OF THE AMMONIUM SULFIDE GROUP CONTAINING COBALT FROM THE HYDROGEN SULFIDE GROUP—MERCURY, LEAD, BISMUTH, COPPER, CADMIUM, ARSENIC, ANTIMONY, TIN, GOLD, MOLYBDENUM, ETC.

Hydrogen sulfide passed through an acid solution containing 5 to 7 ml. hydrochloric acid (sp.gr. 1.2), or 3 to 5 ml. sulfuric acid (sp.gr. 1.84) per 100 ml. precipitates only members of the second group and silver. The separation is by no means clean cut with all the elements of this group, but with those metals commonly met with in industrial laboratory work, it is effective. When hydrochloric acid is used, the acidity of the solution should be no higher than as stated, or the lead and cadmium may not be completely precipitated. In cobalt analysis, where the electrolytic method is almost always preferable, sulfuric acid is commonly used. This offers the advantage that the lead may be almost completely eliminated with the insoluble, and lead is an element frequently associated with cobalt ores. On occasion it may be convenient to use a nitric acid solution, which may be done if kept very dilute, but in cobalt analysis this is outlawed on account of its interference with the subsequent electrolysis.[5]

Separation of the Ammonium Sulfide Group from the Alkaline Earths and Alkalies.—Colorless ammonium sulfide, free from carbonates, added to a neutral solution, from which oxidizing agents are absent, and with sufficient ammonium salts to hold the magnesium in solution, will precipitate the members of the ammonium sulfide group from the alkaline earths and alkalies. The precipitation is seldom complete unless the formation of polysulfides is prevented by the addition of ammonium sulfite. This addition is advisable unless the partial precipitation of the alkaline earths as sulfites is undesirable. A second precipitation should be made if large quantities of the alkaline earths are present.

A convenient point at which to apply this method is after the hydrogen sulfide precipitate has been removed by filtration. To the filtrate, still saturated with hydrogen sulfide gas, ammonium hydroxide is added in excess and the gassing continued. The iron being in the ferrous state, precipitates as the flocculent ferrous sulfide which is easy to filter; and no sulfur being formed by the reduction of ferric iron, no polysulfides are produced from that source. In the filtering of the sulfide precipitate, care should be taken to avoid unnecessary exposure to the air by covering the funnel with a watch glass whenever possible.

Separation of Cobalt and Nickel from Manganese.—*A.* A chloride or sulfate solution, free from second group elements, is treated with an excess of sodium carbonate and then made strongly acid with acetic. About 5 grams of sodium acetate for each gram of cobalt and nickel present is now added, the solution diluted to 200 ml. and heated to about 80° C. It is then saturated

[5] E. Bertrand, Bull. Soc. Chim. Belg., 38, 364–71 (1929), states that cobalt and nickel may be electrolyzed correctly in ammoniacal solution, if the effect of the nitrate ion is counteracted with $Na_2S_2O_3$. In the absence of zinc, a large quantity of sulfite is used and the solution kept cold. In the presence of zinc, little sulfite is used and the solution kept hot.

with hydrogen sulfide gas. Cobalt and nickel are precipitated as sulfides and the manganese remains in solution. The sulfides are filtered off and the filtrate concentrated. Colorless ammonium sulfide is added and the solution rendered acid with acetic. It is then warmed and filtered. This concentration and reprecipitation must be repeated if necessary.

B. Electrolytic.—Cobalt and nickel may be separated from manganese by electrolysis, the cobalt and nickel being plated out and the manganese remaining in solution or deposited at the anode.

C. Sodium Chlorate.—Manganese may be removed from a nitric acid solution of cobalt or nickel by boiling with sodium or potassium chlorate, preferably the former. An excess of chlorate at the end of the operation is essential. The manganese dioxide precipitated may be removed by filtration through an asbestos mat.

For further details see Ford-Williams method under Manganese.

Among the less known, but possibly useful separations of cobalt from manganese, are the following:

Hampe[6] states that potassium bromate is an excellent precipitant for manganese in acid solution.

Von Knorre[7] bases a separation for manganese on the action of potassium or ammonium persulfates in boiling acid solutions.

Kolthoff and Sandell[8] found that with an acid concentration of 0.4 N to 2 N sulfuric acid, precipitation on boiling was complete, using potassium persulfate. Iron interferes, but not seriously, till the ratio of iron to manganese exceeds 100 to 1. They recommend the potassium salt in preference to the ammonium. They also confirm the use of potassium bromate in acid solutions.

Separation of Cobalt from Nickel.—*A. Dimethyl-glyoxime.*—Nickel is removed from the solution by precipitation with dimethyl-glyoxime. The details of the procedure may be found in the Gravimetric Methods for the Determination of Nickel. Cobalt remains in solution.

B. Nitroso-beta-naphthol.—Cobalt is precipitated by nitroso-beta-naphthol, leaving nickel in solution. Details of the procedure are given under Gravimetric Methods for the Determination of Cobalt.

C. Potassium Nitrite.—Cobalt is precipitated as potassium cobalti-nitrite, nickel remaining in solution. Details of the procedure are given under Gravimetric Methods for the Determination of Cobalt.

D. Alkali Xanthates.[9]—A separation of cobalt and nickel has been worked out, based on the relative solubilities of the two xanthates in ammonium hydroxide. To a solution containing the two elements, one gram of citric acid is added and ammonia in excess, then one gram of potassium xanthate and acetic acid. The precipitate of cobalt and nickel xanthates is filtered off and returned to the beaker. It is treated with ammonium hydroxide, filtered and washed with ammonium hydroxide till the washings no longer show a trace of yellow. The nickel is now in solution from which it may be precipitated by acetic acid. The cobalt precipitate is ignited at full red heat to convert it to

[6] Hampe, Chem Ztg., 7, 1106 (1883): 9, 1083 (1885).
[7] Von Knorre, Z. angew. Chem., 14, 1149 (1901); 16, 905 (1903); Chem. Ztg., 27, 53 (1903).
[8] Kolthoff and Sandell, Ind. and Eng. Chem., Anal. Ed. 1, 181, 1929.
[9] Whitby and Beardwood, Chem. & Met. Soc. of South Africa, 21, 199–200 (1921).

Co_3O_4, in which form it may be weighed, or converted to sulfate, neutralized with ammonia and plated.

E. Phenyl-thio-hydantoic Acid.[10]—According to Willard and Hall, this reagent precipitates cobalt completely from As, U, V, Ti, W, Mo, Zn, Cr, Al, Mg, Ca. Ferric iron in the presence of ammonium citrate, contaminates the precipitate slightly. Nickel is precipitated to some extent, but is soluble in concentrated ammonium hydroxide. The cobalt may be determined gravimetrically or volumetrically.

F. Carbonyl[11]—T. M. Lowrey offers a very complete separation of nickel from cobalt by reducing to the metallic state and heating in a current of carbon monoxide. The nickel is volatilized as NiC_4O_4, the cobalt remaining behind.

G. Alpha-benzil-dioxime.[12]—This reagent may be used instead of dimethyl-glyoxime as a precipitant for nickel in the presence of cobalt. The reaction is more delicate, but is only satisfactory for small amounts of nickel. The reagent is much less soluble in alcohol than dimethyl-glyoxime. For further details see chapter on Nickel.

Separation of Cobalt and Nickel from Zinc.—*As the Sulfide.*—Zinc sulfide is precipitated from dilute acetic and formic solutions by hydrogen sulfide. It is also precipitated by the same gas from hydrochloric and sulfuric acid solutions, if the acidity is properly adjusted. Full details are given under Standard Methods for Zinc.

Caldwell and Moyer[13] state that if zinc sulfide is precipitated in the presence of certain aldehydes, particularly acrolein, the amount of cobalt carried down is greatly reduced. This makes it possible to separate zinc and cobalt with one precipitation. This offers some improvement, regardless of the unpleasant odor of the acrolein. They suggest the following procedure:

> "The quantitative procedure adopted for precipitation of zinc sulfide in the presence of cobalt is but slightly different from conventional methods. The pH of a chloride free solution containing 0.25 gram of zinc and cobalt up to 0.5 gram is adjusted until the hydroxides just remain in solution, then 6 to 8 grams ammonium sulfate is added. The total volume is brought to 250 to 300 ml. and 0.2 ml. of acrolein is added. A rapid stream of hydrogen sulfide is passed in at room temperature for thirty minutes. Five to 10 ml. of a 0.02% gelatin solution is added and the precipitate is filtered off after fifteen to twenty minutes standing. Cold distilled water is used to transfer and wash the precipitate. In some cases, the filtrate develops a faint white turbidity after standing. This is due to the formation of a small quantity of resinous acrolein-hydrogen sulfide reaction product. If the filtrate is to be used for further analysis, it is strongly acidified and boiled down to about one-third of its original volume. This treatment will drive out most of the acrolein, and if any still remains, it will appear as small yellow flakes which are readily filtered off."

Separation of Cobalt and Nickel from Chromium.—Cobaltous and nickelous hydroxides precipitated from a sodium hydroxide solution, are oxidized to the black cobaltic and nickelic hydroxides by chlorine, bromine, sodium hypo-

[10] Willard and Hall, J. Am. Chem. Soc., 44, 2219–26 (1922).
[11] T. M. Lowrey, Chem. & Ind., 42, 462–5 (1923).
[12] F. W. Atack, Analyst, 38, 448, 318.
[13] Caldwell and Moyer, J. Am. Chem. Soc., 57, 2375–7 (1935).

chlorite or sodium hypobromite, leaving the chromium in solution as chromate, from which they may be separated by filtration. Ammonium salts must be absent. Details of the separation are given under Stellite in Special Procedures.

Separation of Cobalt and Nickel from Iron.—*A. Electrolysis in the Presence of the Iron Hydroxide.*

B. Repeated Precipitations with Ammonium Hydroxide and Hydrogen Peroxide.—Both methods are discussed under Determination of Cobalt in Ores by Electrolysis.

C. Basic Acetate Separation.—Full details of the procedure to be followed are given in the chapter on Manganese.

D. Rothe's Ether Separation.—Details are given under separations in the chapter on Iron.

E. Precipitation by Zinc Oxide.[14]—An emulsion of zinc oxide, added to an oxidized solution of either chlorides or sulfates, from which the second group has been removed, precipitates iron, aluminum and chromium, leaving cobalt, nickel and manganese in solution. The solution is first rendered neutral to methyl orange with sodium carbonate and the emulsion added in small lots at a time with agitation, till in decided excess. The precipitation is usually carried out in a 1000 ml. volumetric flask and, as soon as the reaction is complete, this is diluted up to the mark. It is allowed to settle for half an hour, then an aliquot portion filtered off. Generally this separation is used in conjunction with the nitroso-beta-naphthol method, which procedure is described under Gravimetric Methods for the Determination of Cobalt.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF COBALT

Precipitation of Cobalt by Potassium Nitrite.—Cobalt may be precipitated from a solution made slightly acid with an excess of acetic acid by adding a hot solution of potassium nitrite. The cobalt is precipitated as potassium cobaltinitrite, $2K_3Co(NO_2)_6 \cdot 3H_2O$, very completely, after standing for a period of six hours. This method has the advantage of making possible the separation of cobalt from nickel and iron, although it has the one disadvantage, for commercial purposes, of requiring a long time to complete the determination.

Oxidizing agents, free mineral acids, members of the hydrogen sulfide group, large amounts of aluminum, iron, trivalent chromium, alkaline earths and ammonium salts should be absent. In the analysis of ores and many other substances, the only point where the absence of these interfering bodies can be assured is after the cobalt and nickel metals have been plated out from an ammoniacal solution.

[14] See Hoffman, Bur. Stds. J. Res., 7, 883 (1931).

Procedure.—The ore or other material to be assayed, having been taken into solution by acids or by fusion, the hydrogen sulfide group removed and the cobalt and nickel plated out from an ammoniacal solution, the deposit is dissolved in nitric acid (sp.gr. 1.4). A weaker acid should not be used as there is danger that the nickel would not be completely dissolved from the cathode. When this happens, the cathode becomes discolored on heating, and this can only be remedied by repeated acid treatments and heating to high temperature. The solution of the nitrates is taken to a syrup and diluted to about 30 ml. with water, then neutralized with potassium carbonate. Two to 3 ml. acetic acid are added and the solution boiled. Fifteen to 20 grams potassium nitrite, free from lead and alkaline earths, are dissolved in 25 ml. water and acidified with 2 ml. acetic acid. This is brought to the boiling point and the hot solution added to the cobalt-nickel solution while briskly stirring. The beaker is kept at the boiling point for half an hour, then, after washing down the walls with a potassium nitrite solution, allowed to stand in a warm place for at least six hours, or preferably over night. It is then filtered through a porcelain Gooch crucible with a fritted bottom, which is connected with an Erlenmeyer filter flask by means of a rubber crucible holder with a funnel attachment which carries the drip past the suction tubulature.

The precipitate is washed six times with a 10% potassium acetate solution, or a 5% potassium nitrite solution acidified with acetic acid, then the crucible is returned to the original beaker. Thirty-five ml. sulfuric acid (1 : 6) are added and after covering with a watch glass, it is warmed till solution is complete. It is then cooled and the crucible raised by means of a suitably bent glass rod and the outside washed with a gentle stream of water. Six washings are then passed through the crucible to insure the removal of cobalt from the fritted bottom. This is accomplished by means of a tight fitting rubber stopper through which passes a glass tube connected to an atomizer bulb. The crucible is half filled with water, the stopper inserted and a gentle pressure exerted by the atomizer bulb. This forces the water through the pores of the fritted bottom into the beaker. The solution is then taken to fumes and fumed dry. It is cooled, 50 to 70 ml. distilled water and 10 ml. sulfuric acid (1 : 1) added and the solution boiled and cooled. Sufficient ammonium hydroxide is then added to neutralize the free acid and an excess of from 50 to 75 ml., according to the cobalt content. It is then plated.

The plating conditions are discussed under Determination of Cobalt in Ores by Electrolysis.

A method alternative to filtering through a fritted bottomed crucible is to filter through a 9 cm. filter paper, washing as above. The paper is then spread on the inside of the original beaker and the precipitate washed off with the minimum amount of water. This is followed by successive washes of sulfuric acid (1 : 6), at a temperature of 70 to 80° C., till the yellow color disappears from the paper. Sometimes there is difficulty in dissolving the potassium cobalti-nitrite with this procedure. In such cases the paper may be returned to the beaker, enough sulfuric acid (1 : 6) added to bring the volume to about 20 to 30 ml. and boiled. Care must be taken to avoid concentrating the acid or the paper will become carbonized; a slight blackening will do no harm. The paper is then filtered off using suction, and washed thoroughly. No cobalt or nickel is retained by the paper. The solution is then taken to fumes and if

any blackening develops, it is cleared up by very cautiously adding a few small pinches of ammonium persulfate. It is then fumed dry and proceeded with as before.

After plating and weighing the deposit of cobalt it should be dissolved in nitric acid and tested for the presence of nickel by the dimethyl-glyoxime method; any precipitate so found being filtered off, dried and weighed, the resulting nickel being deducted from the cobalt figure.

Nickel may be determined in the filtrate from the potassium cobalti-nitrite precipitation, by the direct addition of dimethyl-glyoxime. This may serve for ordinary routine plant control, but a better procedure is to precipitate the nickel as the nickelic hydroxide with sodium hydroxide and bromine, and after filtering and washing, to dissolve in hydrochloric acid. From this point either the dimethyl-glyoxime or the electrolytic method may be applied.

Precipitation of Cobalt by Nitroso-beta-naphthol.[15]—Nitroso-beta-naphthol, $C_{10}H_6(NOH)$, added to a hydrochloric acid solution of cobalt, precipitates cobalti-nitroso-beta-naphthol, $Co(C_{10}H_6O(NO))_3$; nickel, if present, remains in solution. The method is especially suitable for the determination of small amounts of cobalt in the presence of comparatively large amounts of nickel. The cobalt precipitate is voluminous, so that the sample taken for the determination should not contain over 0.1 gram of cobalt. The reagent will also precipitate copper and iron completely from solution. Silver, bismuth, chromium, tin, zirconium, titanium, vanadium and nitric acid interfere, but mercury, lead, cadmium, arsenic, antimony, aluminum, manganese, nickel, calcium, magnesium, beryllium, zinc and phosphates do not.

Procedure.—To the solution containing the cobalt as the chloride or the sulfate, and acidified with 3 ml. hydrochloric acid, or its equivalent of sulfuric, per 100 ml., is added a freshly prepared hot solution of nitroso-beta-naphthol, made by dissolving 10 grams of the salt in 100 ml. of 50% acetic acid, as long as a precipitate is produced. After allowing it to settle, more of the reagent is added to insure complete precipitation of the cobalt. The compound is allowed to settle for two or three hours, the clear solution decanted through a filter and the precipitate washed by decantation with cold water, then with warm hydrochloric acid solution (1 : 2), to remove the nickel, and finally with hot water until free of acid. If nickel greatly predominates, the precipitate should be ignited to oxide in a porcelain crucible, dissolved in hydrochloric acid and reprecipitated.

The brick red precipitate is dried, then ignited in a weighed platinum crucible (Rose crucible), first over a low flame and finally at a white heat, the crucible being covered with a platinum cover (Rose crucible type) with a platinum tube through which is passed a slow current of oxygen. The residue is weighed as Co_3O_4. The oxide may be reduced in a current of hydrogen and weighed as metallic cobalt.

When the amount of cobalt exceeds a few milligrams it is advisable to convert it to sulfate by treatment with HNO_3 and H_2SO_4 and then take to fumes and deposit the element by electrolysis from a sulfate solution.

[15] Burgess, Z. angew. Chem., 9, 596 (1896).

DETERMINATION OF COBALT IN ORES BY ELECTROLYSIS

Typical Analysis of a Cobalt Ore.[16]—The most satisfactory method for the separation of cobalt and nickel from the elements usually associated with them involves the use of electrolysis.

This is generally carried out in a strongly ammoniacal solution, containing sulfates or chlorides. The metals will plate from a weak acid solution, but not quantitatively. Oxalates and acetates may be used, but the results are generally somewhat high.

The minerals of which cobalt and nickel form constituents, are readily soluble in acids and if the sample has been ground to an impalpable powder, the insoluble, after acid treatment, should be free from cobalt. Where this is uncertain, the insoluble is filtered off, washed with hot water and if the presence of lead sulfate is suspected, an ammonium acetate wash followed by hot water is given. It is then ignited in a platinum crucible and fused with either potassium bisulfate or a mixture of sodium and potassium carbonates. The melt is dissolved and returned to the original acid solution.

With the ordinary run of cobalt ore, containing 1% and upwards of cobalt and variable nickel, 0.5 to 1 gram is generally sufficient to take for assay. In the case of ores under 1%, if close work is essential, much greater amounts must be taken, and the large insoluble attacked by the usual procedure of fusion or elimination of the silica by hydrofluoric acid.

Procedure.—One-half to 1 gram is weighed into a 400 ml. beaker and after moistening with water and covering with a watch glass, 10 ml. nitric acid (sp.gr. 1.4) added, taking care to avoid loss through too violent an action. After the reaction has abated, 10 ml. sulfuric acid (1 : 1) are added and the solution taken to fumes. It is then cooled, 0.5 to 1 gram sodium thiosulfate added, in small quantities at a time. The object of this is to reduce the arsenic to the arsenious condition and render its elimination as the chloride as complete as possible. A glass triangle is now put under the watch glass and the beaker taken to fumes and fumed dry. It is then cooled, 50 ml. hydrochloric acid (sp.gr. 1.2) and 10 ml. sulfuric acid (1 : 1) added and again fumed dry. This should remove the arsenic almost completely, which is an advantage in the subsequent gassing out of the hydrogen sulfide group. The prolonged acid treatment nearly always effects complete decomposition of the ore.

The sulfuric acid having been fumed off, 50 ml. sulfuric acid (1 : 20) are added and the solution boiled. A steady stream of hydrogen sulfide gas is passed through the solution till the elements of this group are completely precipitated. The sulfides are removed by filtration and washed with hydrogen sulfide water containing 1 ml. sulfuric per 100 ml.

The filtrate is boiled to expel hydrogen sulfide and oxidized with ammonium persulfate. It is again boiled for ten minutes, cooled, 30 ml. ammonium hydroxide (sp.gr. 0.9) very cautiously added and the solution neutralized with dilute sulfuric acid. Fifty to 70 ml. ammonium hydroxide are added and the solution electrolyzed in the presence of the iron hydroxide. This will be discussed later on.

[16] Method in use in the laboratory of the Deloro Smelting and Refining Co. Limited, Deloro, Ontario, Canada.

The bulk of the solution should not greatly exceed 150 ml. For every 0.25 to 0.3 gram metal present, approximately 5 to 10 grams ammonium sulfate or ammonium chloride and 50 ml. ammonium hydroxide should be in solution. The ammonium hydroxide concentration should be maintained so that the electrolyte is strongly ammoniacal at the finish; otherwise deposits may form at the anode.

During the plating the beaker may be covered with a split watch glass, recessed to fit the electrodes. A square of window glass of suitable size may be cut in half and recessed in the same way, serving the purpose equally well.

Where time is not of primary importance, the plating may be made with stationary electrodes, using a current of 0.2 to 0.3 amps. per square dcm. This generally takes from 12 to 15 hours, but the work can usually be planned so that the plating takes place over night. The use of a rotating anode and gauze cathode greatly decreases the time of plating, by allowing of a freer circulation of the electrolyte, and the use of a higher current. The deposit is firm and bright. The speed of the rotating anode should be 500 to 1000 revolutions per minute, but this depends on the type of electrode used. The current density should be 0.5 to 2.0 amps. per square dcm.

The end of the plating is determined by removing 5 ml. of the electrolyte, and if iron hydroxide is present, filtering and testing the solution with ammonium sulfide. A darkening of the solution indicates that cobalt and nickel are still present. A more sensitive test is the phenyl-thio-hydantoic, which is described under Detection.

It is not desirable to continue plating after it is finished, as the cathode slowly increases in weight from the deposition of platinum dissolved from the anode.

As the deposit is very soluble in the electrolyte, the current should not be cut till the electrolyte is replaced by distilled water. A simpler and equally satisfactory way is to lower the beaker till the electrodes just make contact with the solution. The cathode is then washed down with a stream of water from a wash bottle. The current is then cut and the cathode quickly removed and dipped into a succession of small beakers, containing distilled water After dipping into absolute alcohol, it is ignited and waved to and fro till the flame dies down, after which it is swung back and forth over a free flame, at a sufficient distance to avoid possibility of oxidation. After cooling and weighing, the combined metals are dissolved in nitric acid (sp.gr. 1.4), the cathode washed and removed from the beaker. The solution of the nitrates is then taken to a syrup and diluted to 30 ml. It is neutralized with potassium hydroxide and reacidified with acetic acid, 2 to 3 ml. being added in excess. The cobalt is then precipitated as the potassium cobalti-nitrite, as described under Gravimetric Methods for the Determination of Cobalt.

After plating the cobalt it should be examined for nickel, which is frequently present in small amount. This is done by precipitation with dimethyl-glyoxime, and any nickel so found is deducted from the cobalt figure.

When it is known that the deposit of the combined metals consists of cobalt and nickel only, and no impurities present, the separation by dimethyl-glyoxime is much to be preferred to the potassium cobalti-nitrite method, both in speed and accuracy. The full details of the dimethyl-glyoxime method are given in the chapter on Nickel.

The combined metals are plated out in the presence of the iron hydroxide. Where this is heavy, there may be danger of the cobalt and nickel deposit being slightly contaminated. This, however, is of no consequence, as the impurities are eliminated by the subsequent cobalti-nitrite separation. The probability of cobalt and nickel being held up by the hydroxides has never proved to have foundation, where the electrolyte has been fully plated out. To assure himself on this point, the analyst has only to filter off the hydroxides, redissolve and replate, using a fresh cathode.

There are two alternatives to plating in the presence of the iron. These are:

A. Basic acetate separation of the iron before electrolyzing. This method is given in detail in the chapter on Manganese.

B. Repeated precipitation of the iron with ammonium hydroxide and hydrogen peroxide.

Procedure.—After the group precipitated by hydrogen sulfide has been removed and the gas boiled out of the filtrate 20 ml. hydrogen peroxide (3 vol.) is added, and the solution boiled. The boiling should not be continued for more than a minute or so, or the hydrogen peroxide will be decomposed and the cobalt tend to remain with the iron hydroxide. The beaker is removed from the hot plate and allowed to cool somewhat, then ammonium hydroxide is cautiously added in slight excess. It is once more boiled for a few minutes, then allowed to settle. The supernatant liquid is decanted down to the precipitate through a 15 cm. C S & S No. 595 filter paper, then the precipitate is transferred to the paper as quickly as possible, using hot water. It is washed three times with hot water and drained, then the paper with the precipitate is spread on the inside of the original beaker and washed, first with hot water, then warm sulfuric acid (1 : 3), finally with hot water and discarded. The beaker is returned to the hot plate and the solution boiled till the precipitate is dissolved. The precipitation with ammonium hydroxide and hydrogen peroxide is then repeated. Three, and sometimes four, precipitations in all may be necessary to remove completely the cobalt from the hydroxides. In addition to being somewhat tedious, this method has the disadvantage of producing very bulky solutions, which should be boiled down and the ammonia content adjusted before plating.

Where the iron hydroxide is exceptionally heavy, the bulk of it may be removed by means of the Rothe method, full details of which will be found under Separations in the chapter on Iron.

The electrolytic method tends to give slightly high results on plating over half a gram of the combined metals. This is doubtless due to the occlusion of gas; probably hydrogen. This difficulty does not seriously affect the use of the method on lesser amounts; the error generally falling in the second place of decimals in the percentage. One-half to 2.0 grams sodium bisulfite, added to the ammoniacal solution, counteracts this tendency to some extent, but it has the disadvantage that sulfur is deposited with the metal and must be determined and deducted from the weight of the combined metals.

If there is any difficulty in plating the cobalt and nickel, it may arise from insufficient elimination of the nitric acid. This is unlikely to occur if the acid treatment has been carried out as described. If molybdenum has escaped the hydrogen sulfide precipitation, it may give trouble, in which case, if its presence is suspected beforehand, greater care must be taken to observe the proper

conditions for its elimination, while passing hydrogen sulfide gas. Manganese and zinc have a retarding effect, and chromium, even in small quantities, inhibits the plating altogether. The use of sodium bisulfite counteracts this difficulty with all four elements to some extent, but where chromium is present in considerable amount, a procedure similar to that outlined under Stellite (Special Procedures) should be followed.

Very infrequently organic matter, especially pyridine, may interfere. The ammonium hydroxide is usually to blame for this, although the high grade of this reagent available on the market, is almost a guarantee against this happening. It is caused by the priming over of a still in the manufacture. Its presence may be detected by taking a few ml. sulfuric acid (1 : 3) in a test tube and while cooling under a tap, adding the suspected ammonia, drop by drop till the neutral point is reached. A pungent odor, resembling the smell of a dirty gun barrel is evidence that pyridine is present.

VOLUMETRIC METHODS

Volumetric methods for cobalt do not find so extended a use as the gravimetric, partly because they are still in the formative stage and because that to a much greater extent they require the absence of interfering elements. Nevertheless, a great many workers have published methods which may be successfully applied under the proper conditions. Among such methods are the following:

A. **Perborate Method.**—Nickel and cobalt are oxidized to trivalent oxides and hydroxides by various oxidizing agents, but neither cobalt nor nickel salts of the trivalent state are stable. Both the trivalent hydroxides liberate iodine when treated with acids and potassium iodide, and form nickelous and cobaltous salts, e.g.

$$Co(OH)_3+KI+3HCl=CoCl_2+I+KCl+3H_2O.$$

Cobalt is more readily oxidized than nickel and when oxidized forms more stable compounds. Cobaltic hydroxide may be formed by treating the sulfate with potassium hydroxide and hydrogen peroxide, while nickel is not affected even on boiling with these reagents. This procedure, however, has not been satisfactory, as a method of analysis, on account of the difficulty of removing the excess hydrogen peroxide, which persists in the precipitate even after boiling and prolonged washing.

W. D. Engle and R. G. Gustavson[17] found that the differential oxidation in the presence of potassium hydroxide, by means of sodium perborate may be

[17] W. D. Engle and R. G. Gustavson, J. Ind. Eng. Chem., 8, 901–2 (1916).

satisfactorily accomplished, as the excess of this oxidizing agent readily decomposes on boiling. Advantage is then taken of the reaction stated above and the iodine liberated is titrated with a standard sodium thiosulfate solution.

Landon A. Sarver[18] has offered a modification of this method. He states that the iodometric method is unsatisfactory in the presence of small amounts of ferric iron, and it requires 0.5 to 2 hours for the dissolving of the precipitate. He therefore substitutes ferrous sulfate and titrates with standard potassium dichromate, using barium diphenylamine sulfonate as an inside indicator.

He suggests the carrying out of the work in a 500 ml. Erlenmeyer flask, fitted with a dropping funnel of 35 to 40 ml. capacity, by means of a well paraffined rubber stopper. But as it is difficult to prevent leakages of a little air, to which ferrous hydroxide is very sensitive, an all pyrex apparatus with ground in dropping funnel is preferable.

Procedure.—" The cobalt solution, free from interfering ions and containing at least 5 ml. of 6 N sulfuric acid, and 1 to 2 grams of dissolved sodium perborate, is treated with enough 6 N sodium hydroxide to leave about 10 ml. in excess, whereupon brownish black cobaltic hydroxide precipitates, accompanied by active effervescence; the mixture is boiled for 10 minutes to decompose excess of perborate and displace last traces of oxygen by water vapor, the dropping funnel being placed in position (with the stopcock open) near the end of this period. After the removal from the hot plate the apparatus is promptly closed and an excess of standard ferrous sulfate measured into the funnel; upon opening the stopcock cautiously the solution is drawn in by the reduced pressure inside the flask, taking care that no air is allowed to enter. The funnel is rinsed with two or three portions of water, always avoiding the entrance of air, the vessel is shaken a few seconds and 25 to 30 ml. of 6 N sulfuric acid is admitted, whereupon the precipitate dissolves almost instantly. After cooling to room temperature, the stopcock is opened and the funnel removed and rinsed. About 10 ml. of 25% phosphoric acid and 5 drops of an 0.2% water solution of barium diphenylamine sulfonate are then added and the excess of ferrous iron titrated to the appearance of a violet with standard dichromate. The method is extremely rapid.

Interfering ions. Nitrates and other oxidizing substances which give colorations with barium diphenylamine sulfonate, must be absent. Nickel does not interfere. Cobalt can be easily separated in one operation from manganese, chromium, vanadium, etc., by means of phenyl-thio-hydantoic acid. Small amounts of iron are carried down with this precipitate, but not enough to cause incomplete oxidation of the cobalt by the perborate."

Since one $K_2Cr_2O_7 = 6I = 6Co = 6Fe$, then the potassium dichromate factor of the solution multiplied by 1.2020 gives the cobalt factor, or the iron factor multiplied by 1.0555 gives cobalt.

B. **Potassium Cyanide Method.**—This method which is of great value in the estimation of nickel in nickel steel, German Silver and nickel mattes, may be applied equally well to cobalt. But as the conditions of its application require the removal of nickel and other interfering ions, it offers no advantage over other standard methods for the determination of cobalt. Details of the Procedure for Determining Nickel by this method will be found in the chapter on Nickel.

[18] Landon A. Sarver, Ind. Eng. Chem., Anal. Ed. 5, 275–6 (1933).

Other Methods.—A. G. A. Barbieri[19] states that when cobaltinitrites are decomposed by $NaHCO_3$, $NaNO_2$ and a trivalent carbonate of cobalt are formed. On adding $KMnO_4$ in H_2SO_4 solution, the HNO_2 is oxidized to HNO_3 and cobaltic cobalt reduced to cobaltous, so that for each atom of cobalt, 11 equivalents of $KMnO_4$ are reduced. Standard $FeSO_4$ is added in excess and titrated with $KMnO_4$.

B. P. V. Faleev[20] dissolves the potassium cobaltinitrite in H_2SO_4 and a measured volume of $KMnO_4$ solution. He reduces the excess $KMnO_4$ with oxalic acid and titrates the excess with $KMnO_4$.

C. Christo Nikolow[21] dissolves the potassium cobaltinitrite in H_2SO_4 and standard $KMnO_4$, adds KI and titrates excess iodine with $Na_2S_2O_3$. The method, it is claimed, is well suited for cobalt in steels, because other metals do not interfere.

D. J. T. Dobbins and J. P. Sanders,[22] base an indirect titration method on Spacu's[23] pyridine precipitation.

Spacu and Dick have shown that when a cobaltous salt is treated with alkali thiocyanate and an excess of pyridine, a precipitate, $CoPy_4(SCN)_2$, containing 12.01% Co is formed.

Dobbin and Sanders add to the solution, containing 0.05–0.10 grams Co or Ni, HNO_3 till acid, then 3 ml. pyridine and a measured volume of NH_4CNS. The solution is diluted to 250 ml. and filtered through a dry filter paper. An aliquot portion of 50 ml. is taken, diluted to 100 ml., one ml. HNO_3 added and an excess of standard $AgNO_3$ run in. Five ml. ferric alum is added and titrated in the usual way.

Cobalt and Nickel may be determined in the same solution, by precipitating them as the complex pyridine salts as outlined, determining the nickel by the glyoxime method and calculating the cobalt by difference.

SPECIAL PROCEDURES

BLACK AND GRAY COBALT OXIDES

Procedure.—One gram is weighed into a 400 ml. beaker and 25 ml. hydrochloric acid (sp.gr. 1.2) added. The beaker is covered with a watch glass and kept simmering gently on the hot plate till the acid is almost all expelled and the oxide appears to be in solution. A glass triangle is put under the watch

[19] G. A. Barbieri, Atti Accad. Lincei, 8, 405–8 (1928).
[20] P. V. Faleev, Gorno-Obogatitelnoe Delo, 10, 53–4 (1932).
[21] Christo Nikolow, Przemsl Chem., 17, 46–8 (1933).
[22] J. T. Dobbins and J. P. Sanders, Ind. Eng. Chem., Anal. Ed. 6, 459–60 (1934).
[23] G. Spacu and J. Dick, Z. anal. Chem., 71, 97–101 (1927).

glass and the solution taken to dryness, at a temperature well under the boiling point. Ten ml. sulfuric acid (1 : 1) is then added, taken to fumes and fumed dry. It is then taken up with 10 ml. sulfuric acid (1 : 1) and heated, then 60 ml. hot water added and boiled. At this point, the oxide should be completely in solution and the insoluble pure white. If this is not the case, or if the insoluble is large in quantity, it must be filtered off and ignited. It is then treated with hydrofluoric acid and a few drops sulfuric acid in a platinum basin, to expel the silica. After fuming it is cooled, diluted and added to the main solution. If preferred, a fusion with potassium bisulfate or with a mixture of sodium and potassium carbonates, may be made instead of the hydrofluoric acid treatment.

A stream of hydrogen sulfide gas is passed through the solution and the precipitate filtered off and washed with hydrogen sulfide water containing 1 ml. sulfuric acid in 100 ml. solution. After boiling out the hydrogen sulfide gas, the solution is oxidized by the addition of ammonium persulfate and boiled for ten minutes. It is cooled, neutralized with ammonium hydroxide, 70 ml. added in excess and electrolyzed, in the presence of the iron hydroxide precipitate. The end of the plating is determined by withdrawing 5 ml. of the solution and after filtering, testing with either ammonium sulfide or phenyl-thiohydantoic acid. (See Detection.)

The deposit of cobalt and nickel is dissolved in nitric acid (sp.gr. 1.4), and after the cathode has been washed and removed, the solution is taken to a syrup. It is then diluted with water and carefully neutralized with sodium hydroxide, and rendered acid with hydrochloric acid, leaving a few drops in excess. From 10 to 20 ml. of a 50% sodium acetate solution is added and the solution boiled and allowed to stand a few minutes to permit any iron which may have plated out, to show. This must be filtered off and determined, the resulting iron being deducted from the combined metals. Five grams ammonium chloride is now added to the solution and the nickel precipitated with dimethyl-glyoxime. The resulting precipitate is filtered off through a Gooch crucible, washed, dried and weighed. The weight multiplied by 0.2032 gives the weight of the nickel. This deducted from the combined weight gives the cobalt.

COBALT IN METALLIC COBALT

Cobalt in metallic cobalt is usually determined electrolytically. The procedure is similar to that outlined for cobalt oxides, except that nitric instead of hydrochloric acid is used for dissolving the sample, the nitric acid being afterwards expelled by fuming with sulfuric acid.

The plating may be conducted in the presence of the iron precipitate if any small amount of iron deposited with the combined metals is determined and deducted.

The nickel is determined in the deposit by dimethyl-glyoxime in the usual way.

The method is satisfactory for ordinary routine works control but where very pure metals, such as electrolytic cobalt and nickel, must be analyzed closely, it tends to give slightly high results, probably due to the occlusion of hydrogen. In such cases it may be better to determine the impurities and make a deduction from 100% for the cobalt figure or nickel figure, as the case may be.

COBALT IN FERRO-COBALT

Usually this material contains from 20 to 30% iron, the remainder being cobalt and extraneous elements.

Procedure.—One-half gram is weighed into a 400 ml. beaker and dissolved in 10 ml. nitric acid (sp.gr. 1.4). When the action has ceased 10 ml. sulfuric acid (1 : 1) is added and the solution taken to fumes and fumed dry. Fifty ml. sulfuric acid (1 : 20) is added and the solution boiled till the sulfates are all dissolved. A steady stream of hydrogen sulfide gas is passed through the solution to remove the second group elements and after filtering, the gas is boiled out of the filtrate. Ammonium persulfate is added to oxidize the solution and boiling is continued for ten minutes. If manganese is present, potassium persulfate should be used instead of the ammonium salt, and the precipitated manganese dioxide removed by filtration through an asbestos mat.

The solution is cooled, neutralized with ammonium hydroxide and 50 ml. added in excess. As there may not be sufficient ammonium salts present in the solution, 5 to 10 grams ammonium sulfate is added. The solution is then electrolyzed in the usual way in the presence of the iron hydroxide, making the necessary correction for any iron plated with the combined cobalt and nickel.

Nickel in the deposit is determined by the dimethyl-glyoxime method.

The alternatives to plating in the presence of the hydroxide precipitate are:

A. Basic Acetate Separation. (See chapter on Manganese.)

B. Precipitation of the Iron as Hydroxide by Means of Ammonium Hydroxide and Hydrogen Peroxide. (See Determination of Cobalt in Ores by Electrolysis.)

C. Rothe's Ether Separation. (See chapter on Iron.)

D. Zinc Oxide Separation followed by Nitroso-beta-naphthol. (See under Separations, also American Society for Testing Materials Method for Cobalt in Steels in this section.)

E. Cupferron.—The iron may be removed by precipitation in the cold from a 10% hydrochloric or sulfuric acid solution, by the addition of a 6% aqueous solution of cupferron. This requires the destruction of the organic compound with nitric acid, and fuming with sulfuric acid, before proceeding with the electrolysis. The details of the cupferron precipitation are given in the chapter on Iron.

DETERMINATION OF COBALT IN METALLIC NICKEL

Where the cobalt content of the metal is 1% or more, one gram is a sufficient amount to take for assay. The general procedure for metallic cobalt may be followed till the nickel and cobalt metals have been plated out from an ammoniacal solution. The usual separation of the cobalt may be made by precipitating as potassium cobalti-nitrite, as described under Gravimetric Methods for the Determination of Cobalt.

If, however, the cobalt percentage is very low, necessitating the taking of a large sample for assay, the following method may be used:

Procedure.—Five grams of the thoroughly mixed drillings are dissolved in the minimum amount of nitric acid (1 : 1). The solution is taken to a syrup, but the evaporation is not carried far enough to cause the decomposition of the

nitrates. Fifty ml. of water is added and the nitrates brought into solution. A saturated solution of potassium hydroxide is added till a small but definite permanent precipitate forms. This is redissolved with acetic acid (1 : 1) and 10 ml. added in excess. The solution is heated to boiling and 10 ml. of a 50% potassium nitrite solution, which has been rendered acid with acetic, is added. The solution is stirred briskly while adding the potassium nitrite solution. After allowing to stand for half an hour, just under the boiling point, the walls are washed down with a 1% solution of potassium nitrite containing 1 ml. glacial acetic per liter. The precipitate is then settled for six hours or preferably over night.

The solution is filtered out through a fritted bottomed porcelain crucible, using suction and, after washing, dissolved in sulfuric acid and taken to fumes.

It is diluted and a stream of hydrogen sulfide gas passed to remove any trace of the second group elements which may have been occluded by the precipitate. After filtration the gas is boiled out and the solution oxidized with ammonium persulfate. It is then neutralized with ammonia, excess added and electrolyzed. (For full details see Determination of Cobalt in Ores by Electrolysis.)

By this procedure, all the cobalt in the sample will be recovered in the plating, but it will be slightly contaminated with nickel. This must be determined by the dimethyl-glyoxime method and the amount deducted from the cobalt figure.

METHOD OF THE AMERICAN SOCIETY FOR TESTING MATERIALS

DETERMINATION OF COBALT BY THE ZnO–α–NITROSO–β–NAPHTHOL METHOD

Special Solutions Required

ZnO Suspension.—Add 50 g. of the finely powdered reagent to 300 ml. of water and shake thoroughly.

α-Nitroso-β-Naphthol.—Dissolve 1 g. of the dry reagent in 15 ml. of glacial acetic acid and filter.

Procedure.—*Cobalt Steel.*—Transfer 1 g. of sample to a 400 ml. beaker, add 25 ml. of diluted HCl (1 : 1), heat, and when decomposition is complete, add 5 ml. of diluted HNO_3 (1 : 1), to oxidize the iron. If tungsten is present the digestion with HNO_3-HCl must be continued until all of the tungsten has been converted to yellow tungstic acid. Evaporate until salts begin to separate (about 5 ml.). Add 100 ml. of hot water, and digest on the steam bath for about five minutes. Dilute the solution to about 200 ml., and add a freshly

prepared suspension of zinc oxide in portions of about 5 ml. until the iron is precipitated, and a slight excess of zinc oxide is present. Shake thoroughly after each addition of the precipitant and avoid a large excess. When sufficient zinc oxide has been added, further addition of the reagent causes the brown precipitate to appear lighter in color upon thorough shaking. A sufficient excess is also indicated by a slightly white and milky supernatant liquid. Allow the precipitate to settle for a few minutes, and filter the solution through a 12.5 cm. rapid filter paper.[24] Wash the beaker and the precipitate on the filter three times with cold water. Reserve the filtrate and washings. When the filter has drained, transfer the paper and precipitate to the beaker in which the precipitation was made, add 12 ml. of HCl, and stir the paper to a pulp. The iron should now be in solution; if it is not, add more HCl, avoiding a large excess. Dilute the solution to 200 ml., and repeat the precipitation with zinc oxide. Filter on a 15 cm. paper, and wash 4 or 5 times with cold water.

For routine work, a single precipitation will often suffice. In this case take a 2 g. sample, dilute the solution to exactly 500 ml. after the addition of ZnO, mix thoroughly and filter through a dry filter into a 250 ml. measuring flask ($\approx$ 1 g. sample). With one precipitation by ZnO, results for cobalt in high-speed steels will be from 0.1 to 0.3 low through retention of cobalt by the bulky precipitate.

To the combined filtrates and washings, from the zinc oxide separation, add 10 ml. of HCl, and adjust the volume to about 400 ml. Heat the solution to boiling, add 8 ml. of α-nitroso-β-naphthol solution plus 3 ml. in addition for every 0.01 g. of cobalt present. Allow the solution to cool for one-half hour or more, and filter through rapid paper. Transfer all of the precipitate to the filter and wash with hot diluted HCl (1 : 3) and then thoroughly with hot water.

Transfer the wet paper and precipitate to a weighed porcelain crucible, heat gently at first, preferably in a muffle furnace, and finally ignite to constant weight at 750° to 850° C. Heating above 900° C. has a tendency to convert Co_3O_4 to CoO. Cool and weigh as Co_3O_4 which contains 73.4% of cobalt. In very accurate work in which more than 0.01 g. of cobalt is involved, the oxide must be reduced by hydrogen, cooled in an atmosphere of hydrogen, and the cobalt weighed as metal.[25] Nickel accompanies cobalt almost completely in the zinc oxide separation. Hence, in very accurate work, when nickel preponderates, or much of it is present, the ignited cobalt oxide should be dissolved in HCl and cobalt again precipitated with α-nitroso-β-naphthol.[26]

A blank should be taken through all steps of the determination. A 1 g. sample of National Bureau of Standards Bessemer steel 10d or chrome-tungsten-vanadium steel No. 50a is satisfactory for this purpose. It is especially important that the same quantity of the α-nitroso-β-naphthol be used in the blank run as in the determination. A little macerated paper added to the blank after the α-nitroso-β-naphthol reagent facilitates filtration and washing.

[24] A little finely divided ZnO may pass through the paper at first. This is unobjectionable, because zinc is not precipitated by α-nitroso-β-naphthol.

[25] With high molybdenum or copper steels (1%), the ignited Co_3O_4, or cobalt metal may contain small amounts (approximately 0.5 mg.) of these elements. Suitable corrections can be made after solution of the residue and colorimetric determinations of the contaminants.

[26] Tests on a 0.5 sample of a steel containing 10% of cobalt and 6% of nickel showed but 0.1 mg. of nickel in the first precipitate.

Plain Carbon and Other Steels Containing Less than 0.10 % Co.—Dissolve a 10 g. sample in HCl and cautiously oxidize with just enough HNO_3. Extract the iron with ether and wash the ether extract once with diluted HCl (p. 465). Warm the ether-extracted acid solution to expel residual ether, and oxidize with $KClO_3$. Dilute to 200 ml., and precipitate twice with ZnO as directed in the method (p. 324). In material containing very little cobalt, it is advantageous to combine the extracted acid solution obtained in ether separations of a number of separate 10 g. samples.

Cast Iron.—Proceed as in plain carbon steels.

Open Hearth.—Proceed as in plain carbon steels.

Wrought Iron.—Proceed as in plain carbon steels.

ANALYSIS OF STELLITE

Cobalt Alloy of Chromium and Tungsten

The alloy Stellite is used for cutlery, surgical instruments, cutting tools and for stelliting or surfacing machine parts subject to mechanical or chemical action. It holds its cutting edge at high temperature and is not easily attacked by acids or alkalies.

The great insolubility of this alloy requires that it be reduced to a fine state of division before any attempt be made to attack, either by fusion methods or by acid treatment. This reduction should, if possible, be made in a stellite mortar, as the amount abraded from a steel mortar would seriously contaminate the sample.

Once reduced to the necessary degree of fineness, preferably past 100 mesh, there are several methods of attack open to use.

1. Fusion with sodium peroxide in a nickel crucible. This procedure, however, precludes the possibility of determining nickel.

2. Fusion with sodium peroxide in an Armco iron crucible. A suitable method where chromium is to be determined quickly.

3. Fusion with potassium bisulfate in a porcelain crucible. In addition to filling the solution with undesirable salts, this has the disadvantage of forming difficultly soluble chromium salts which render subsequent operations troublesome.

4. Treatment with hydrochloric acid (sp.gr. 1.2). This is conducted at a temperature just under boiling, maintaining the volume by frequent additions of the acid. Complete solution is seldom attained, even after three or four hours of treatment, and the insoluble must be fused in platinum, with sodium and potassium carbonates and a pinch of potassium nitrate. This last to be used with caution on account of its action on the platinum.

5. Treatment with perchloric acid, 60%. This offers the most satisfactory reagent so far discovered, for attacking stellite, and by its use the following method, suitable for routine works analysis, has been devised.

Procedure.—One-half gram is weighed into a 300 ml. beaker and 10 ml. perchloric acid (60%), with 10 ml. water, added. The beaker is covered with a watch-glass and boiled on the hot plate till perchloric fumes appear. The watch glass is then removed till all the water has been expelled and the solution fumes strongly. If this is not done, there is danger of water, condensed on

the watch-glass, dropping back into the solution and causing loss by spattering. After the water is gone, the watch-glass is returned and the solution boiled for twenty minutes. It is then diluted to about 75 ml. with hot water, stirred and allowed to settle at the edge of the plate, for one hour. The solution is then filtered through an 11 cm. Whatman paper No. 44 (ash 0.00006 gram) and WO_3 washed with hot hydrochloric acid (1 : 20), till the washings are colorless, when a final wash of cold water is given.

The precipitated tungsten and undissolved material is washed back into the original beaker, 5 ml. ammonium hydroxide (sp.gr. 0.9) is added and the solution boiled till the tungsten is dissolved, and the iron, if present, coagulated. It is then filtered through the same paper and the filtrate caught in a tared platinum basin of 100 ml. capacity. The residue in the filter paper is washed with hot water and the basin put on the hot plate to evaporate down as rapidly as is consistent with safety. The filter paper is then spread on the inside of the beaker and the residue washed down with a jet from a wash bottle, containing hot hydrochloric acid (1 : 3), and finally with water. The paper is folded and put into a platinum crucible which is placed on the hot plate. The perchloric treatment is repeated on the residue, the acid solution going to the main filtrate, the ammonia extract to the platinum basin and the filter paper to the platinum crucible. Generally two treatments are sufficient to effect complete solution, but if not, a third must be undertaken.

Silicon and Tungsten.—The two filter papers are ignited in the platinum crucible and the ash added to the platinum basin, which meanwhile should have evaporated to a few ml. Ten ml. hydrochloric acid (sp.gr. 1.2) is added and after covering with a watch glass and triangle, the evaporation is continued to dryness. It is then ignited at a high temperature, cooled and weighed; the increase in weight being recorded as SiO_2 and WO_3. It is then treated with 7 ml. hydrofluoric acid and a few drops of sulfuric acid (1 : 1), fumed, ignited, cooled and weighed. The loss is taken as SiO_2. This weight multiplied by the factor 0.4672 gives the weight of silicon. By deducting the weight of the silica, SiO_2, from the combined weight, the WO_3 figure is obtained. This multiplied by 0.7931 gives the weight of the tungsten in the sample.

If the sample contains any considerable amount of molybdenum, the SiO_2 and WO_3 precipitate may be contaminated, in which case, after the SiO_2 has been eliminated by hydrofluoric acid and the resulting WO_3 weighed, it is fused with sodium and potassium carbonates, extracted with water and the insoluble, if any, filtered off. Such insoluble generally consists of iron and traces of cobalt. The amount seldom is equal to 0.2%, but for accurate work it should be ignited and the result deducted from the WO_3 figure. The solution is neutralized with sulfuric acid (1 : 1) and boiled to expel carbon dioxide. Three to 5 grams tartaric acid are then added and the solution made ammoniacal with 3 to 5 ml. in excess. Hydrogen sulfide gas is passed to saturation and it is then acidified with sulfuric acid (1 : 1), with 2 ml. in excess for every 100 ml. solution. The gassing with hydrogen sulfide is then continued. This procedure of gassing in both acid and alkaline solution has proved to be the most successful for precipitating molybdenum, under the conditions outlined. The precipitate is collected in a 9 cm. ashless filter paper, washed with a hydrogen sulfide solution, containing 10 ml. sulfuric acid and 10 grams tartaric acid per

litre. It is then burned to MoO_3, cooled and weighed and the weight deducted from the weight of the WO_3.

Copper, Cobalt, Nickel, Manganese, Iron and Chromium.—The filtrates from the perchloric acid treatments are combined, rendered alkaline by the addition of a 25% solution of sodium hydroxide, and enough added in excess to make approximately 2% sodium hydroxide. Chlorine gas is passed through the solution, in the cold, till the cobaltous hydroxide is changed to the black cobaltic hydroxide; this takes only a few minutes and it is not advisable to over-gas. Occasional stirring during gassing is a distinct help. A convenient way of generating the chlorine, where a tank is not available, is to allow hydrochloric acid, under control, to drip on to bleach powder. The precipitate is allowed to settle, filtered through a 15 cm. C S & S No. 604 filter paper and washed with hot water till the washings are colorless. It is drained as dry as possible, then the paper and the precipitate are withdrawn from the funnel and spread on the inside of the beaker. It is washed down with hot water and the paper thoroughly washed with boiling hydrochloric acid (1 : 3) from a wash bottle. The paper is given a final wash with hot water and discarded. The beaker is then heated till the precipitate dissolves, cooled and the precipitation as cobaltic hydroxide repeated If washed well each time, two precipitations are generally sufficient to separate the copper, cobalt, nickel, manganese and iron from the chromium, which last is left in the oxidized state.

The precipitate is dissolved as before in hot hydrochloric acid (1 : 3), 10 ml. sulfuric acid (1 : 1), added, taken to fumes and fumed dry. It is taken up with sulfuric acid (1 : 99), boiled and a steady stream of hydrogen sulfide gas passed to remove the copper. The precipitate is filtered and determined by the iodide or other appropriate method.

The hydrogen sulfide is expelled from the solution by boiling and the iron oxidized with ammonium persulfate. If manganese is present, it will be evident at this stage as the black manganese dioxide, which may be removed by filtration through an asbestos mat. If it is desired to estimate the manganese, potassium persulfate should be used instead of the ammonium salt. The solution must be boiled to effect complete precipitation of the manganese which after filtration may be determined by the bismuthate or other suitable method.

After oxidation and removal of manganese, the solution is cooled, neutralized with ammonium hydroxide (sp.gr. 0.9), 50 to 60 ml. added in excess, 5 to 10 grams ammonium sulfate added and the solution electrolyzed in the presence of iron, in the usual way.

The end of the electrolysis is determined by removing a few ml. and after filtering, to test with phenyl-thio-hydantoic acid.

The combined cobalt and nickel metals plated on the cathode are dissolved in nitric acid (sp.gr. 1.4) and the solution taken to a syrup, diluted, the free acid neutralized with sodium hydroxide, reacidified with hydrochloric acid, sodium acetate added and after boiling allowed to stand for a few minutes. If any iron has been deposited with the cobalt and nickel, it will now be seen and must be filtered off through an ashless filter paper, washed and ignited to Fe_2O_3, and determined, the iron being deducted from the combined weight. Generally the figure is negligible. In the filtrate the nickel is precipitated with a 1% alcoholic solution of dimethyl-glyoxime. The precipitate is filtered off through a Gooch crucible, washed with hot water, and after drying at 120° C., weighed.

The weight multiplied by 0.2032 equals nickel. This figure deducted from the combined weight gives cobalt.

The iron hydroxide suspended in the electrolyte is removed by filtration using a 9 cm. paper and, after washing, dissolved in hydrochloric acid, reduced with stannous chloride, excess mercuric chloride added, then 5 to 6 ml. phosphoric acid and a few drops di-phenyl-amine and titrated with either N/10 ceric sulfate or N/10 potassium dichromate.

Chromium.—The filtrates from the chlorine separation are transferred into a 1500 ml. Griffin type beaker. If the bulk exceeds 500 ml., it is evaporated down to that volume. It is then acidified with sulfuric acid (1 : 1) and 10 ml. added in excess for every 100 ml. of the solution. A few glass beads are added and the solution boiled strongly till the chlorine is completely expelled; as shown by starch iodide paper. It is cooled, 5 to 7 grams potassium iodide added and titrated with N/2 sodium thio-sulfate solution, using starch as an indicator towards the end of the titration.

A slightly more rapid as well as more accurate method for chromium alone, is as follows:

One-half gram is fused in an Armco iron crucible of 50 ml. capacity, with 12 to 15 grams sodium peroxide. On completion of the fusion and before the crucible is too cold, it is tapped on an iron plate to loosen the cake, which is then transferred to a beaker and dissolved in water. The crucible is washed into the beaker and the pulp boiled for ten minutes to remove all oxygen. The solution is then filtered through a Buchner funnel, using suction and the residue washed with a hot 2% sodium hydroxide solution, followed by hot water, till the washings are colorless. The solution is diluted to 500 ml., acidified with sulfuric acid, excess added, cooled to room temperature and the iodide method applied as described above.

Molybdenum and tungsten do not interfere with the iodide titration, but if vanadium is present, the blue end point recurs, giving indefinite results; in which case the ferrous sulfate and permanganate method must be used. (See chapter on Chromium.)

Molybdenum.—One-half gram is weighed into a 300 ml. beaker and the perchloric and ammonium hydroxide treatment given as before, collecting the ammonium filtrates in a beaker. To the perchloric acid solution, sodium hydroxide is added to neutralization and sulfuric acid (1 : 1) to an excess of 1 to 2 ml. per 100 ml. of solution. Through the cold solution hydrogen sulfide gas is passed, raising the heat to help coagulate the precipitate. The precipitated sulfides are removed by filtration using a 9 cm. ashless filter paper, washed with hydrogen sulfide water containing a little sulfuric acid, and reserved. To the ammoniacal solution 3 to 5 grams tartaric acid is added and the solution adjusted to contain 3 to 5 ml. ammonium hydroxide in excess. Hydrogen sulfide gas is now passed to saturation and any precipitate forming, filtered off. The solution is then acidified with sulfuric acid (1 : 1), leaving an excess of 1 to 2 ml. per 100 ml. The gas is again passed for a few minutes and the precipitate removed by filtration using a 9 cm. ashless filter paper, and washed with H_2S water containing 10 ml. H_2SO_4 and 10 grams tartaric acid per 1000 ml.

The two filter papers are then ignited and weighed as MoO_3. This is fused with fusion mixture, dissolved in water, acidified with acetic acid and the

molybdenum reprecipitated as lead molybdate, $PbMoO_4$, which is filtered through a Whatman No. 44, 11 cm. paper, ignited and weighed.

Weight multiplied by 0.2614 equals Molybdenum.

Carbon.—This determination is conducted along the general lines recommended for steel; the train arrangement being similar. The use of high temperature furnaces is preferable.

The sample need not be crushed to a finer degree than 40 mesh and this may be done in a steel mortar. The use of accelerators, such as, lead peroxide, black copper oxide, Armco iron or tin in a fine state of division is essential. Owing to the high carbon content of some stellites, precaution should be taken to prevent low results, caused by the rapid flow of gas through the absorption tube, carrying away water resulting from the reaction. This can best be done by increasing the amount of the desiccant above the absorbant in the tube.

Cobalt in Ores and Enamels [27]

The determination of cobalt in ores and enamels is usually made by a slight variation of the above methods. The silica is separated in the usual manner by taking down to dryness with hydrochloric acid and the warmed solution is treated with hydrogen sulfide to precipitate sulfides insoluble in acid solution. Aluminum, chromium and iron are precipitated by adding ammonium hydroxide to the oxidized solution. In the enamel industry it has been the practice to follow R. W. Landrum's method, in which the cobalt, manganese and nickel are precipitated together as sulfides and filtered off. The manganese is dissolved from this precipitate with cold hydrogen sulfide water acidified with one-fifth of its volume of hydrochloric acid (sp.gr. 1.11). The residue of cobalt sulfide is burned in a porcelain crucible, dissolved in aqua regia and evaporated with hydrochloric acid. The platinum and copper, if they are present, are thrown down by passing hydrogen sulfide through the solution. The filtrate is made ammoniacal and the cobalt is precipitated with hydrogen sulfide. This is filtered off and washed with water containing a small quantity of ammonium sulfide. The precipitate is either ignited and weighed as oxide or reduced in hydrogen to metallic cobalt, taking care to cool it thoroughly in an atmosphere of hydrogen before allowing it to come into contact with the atmosphere of the room, as finely divided cobalt is decidedly pyrophoric and oxidizes readily, particularly if reduced at a low temperature.

Instead of igniting the sulfide precipitate it may be dissolved in hot (1 : 1) sulfuric acid solution with the aid of a little nitric acid and treated as described under Precipitation of Cobalt by Electrolysis.

Cobalt in Steel

This determination is a modification of the nitroso-beta-naphthol method already described, as worked out in the laboratory of the Firth Stirling Steel Co., McKeesport, Pa. The procedure as described by Mr. Giles, Chief Chemist, is as follows:

Two grams of the sample are weighed into a 500 ml. Erlenmeyer flask and dissolved in 50 ml. of concentrated hydrochloric acid. When the sample is completely decomposed 10 ml. of concentrated nitric acid are added to oxidize

[27] R. W. Landrum, Trans. Am. Cer. Soc., 12, 1910.

the iron, tungsten, etc. The solution is evaporated to 10 ml.; 50 ml. of water are added; the contents of the flask are then transferred to a 500 ml. volumetric flask and cooled to room temperature. A fresh solution of zinc oxide is added in slight excess, the contents of the flask diluted to the mark, well mixed, transferred back to the original Erlenmeyer flask and allowed to settle. Filter 250 ml. (equivalent to 1 gram of the sample) through a dry filter paper, transfer it to a 500 ml. flask, then add 6 ml. of concentrated hydrochloric acid.

The solution, which should now be between 300 and 350 ml. in volume, is heated to boiling and 10 ml. of freshly prepared solution of nitroso-beta-naphthol (1 gram of salt to 10 ml. glacial acetic acid) are added for each 0.025 gram of cobalt present. Continue to heat for two minutes, remove from plate, shake well, and set aside until the bright red precipitate settles, which will only take a few minutes. Filter the hot solution and wash the flask out with hot (1 : 1) hydrochloric acid. Wash the paper alternately with hot (1 : 1) hydrochloric acid and hot water until it has been washed five times with the acid, then wash ten times with hot water. The precipitate is transferred to a quartz or porcelain crucible, heated gently to expel the carbonaceous matter, then at a high temperature until ignition is complete. After cooling, the crucible is weighed and the weight of the residue (Co_3O_4) is multiplied by 0.734 to obtain the percentage of cobalt present. If desired, the Co_3O_4 may be reduced in hydrogen and weighed as metal.

Sulfide Pyrophosphate Method (Dufty).—Cobalt is precipitated as sulfide and this is converted to ammonium cobalt phosphate. The precipitate is filtered and washed, then ignited and the cobalt weighed as pyrophosphate. Traces of cobalt passing into the filtrate are recovered by precipitation as sulfide. This is filtered off, ignited to oxide and added to results obtained. (Oxide is Co_3O_4.)

Cobalt in Cobalt Oxide [28]

One gram of finely ground cobalt oxide is either fused with 10 grams of potassium bisulfate or heated with 20% sulfuric acid until dissolved. If the fusion method is used the melt is extracted with water and acidified with sulfuric acid. Arsenic and copper are precipitated by passing hydrogen sulfide, for about one hour, through the warmed solution, which should be diluted to about 200 ml. These are removed by filtration and the cobalt determined by one of the above methods. The following procedure is one of the most satisfactory.

Procedure.—If it is desired to determine the nickel separately, as is usually the case, this is first precipitated with dimethyl-glyoxime as described in the chapter on Nickel, after boiling the solution to expel hydrogen sulfide. It is then evaporated to fumes of sulfur trioxide and taken up with twice its volume of water. The free acid is neutralized with ammonium hydroxide and an excess of 50 ml. of concentrated ammonium hydroxide added. The solution is made up to 250 ml. and electrolyzed as under Precipitation of Cobalt in Ores by Electrolysis.

[28] R. W. Landrum, Proc. Am. Ceramic Soc., 12, 1910.

COLUMBIUM AND TANTALUM [1]

Symbol Cb, ***at.wt.*** **93.1;** ***sp.gr.*** **8.4;** ***m.p.*** **1950° C.;** ***oxides:*** **Cb_2O_3, Cb_2O_5**
Symbol Ta, ***at.wt.*** **181.5;** ***sp.gr.*** **16.6;** ***m.p.*** **2900° C.;** ***oxide:*** **Ta_2O_5**

Occurrence.—The only ores of commercial importance are tantalite, the tantalum-rich member of the isomorphous tantalite-columbite series (Ta, Cb)$_2$O$_5$·(Fe, Mn)O, and columbite. The chief deposits of high-grade tantalite (Ta_2O_5 over 60%) occur in Western Australia, while columbite carrying up to about 40% Ta_2O_5 is produced in South Dakota. The specific gravity decreases with the tantalum content from 7.8 for tantalite to 5.3 for columbite. The tantalum content of pure specimens of the ore may be roughly estimated (within 5%) by determination of its specific gravity and reference to Simpson's Table given below. Up to the present, columbium was considered an undesirable constituent of tantalum ore, not because it exerts any harmful effects, but because it decreases the yield of tantalum while increasing the consumption of chemicals.

SIMPSON'S TABLE

(Bull. 23, W. Austral. Geol. Survey, 1906, 72.)

Sp.gr.	% Ta_2O_5 in ferrotantalite	% Ta_2O_5 in manganotantalite
5.3	trace	2
5.5	6	10
5.7	14	19
5.9	22	27
6.1	30	36
6.3	38	44
6.5	45	51
6.7	52	59
6.9	59	66
7.1	65	72
7.3	70	78
7.5	75	83
7.7	79	—
7.9	84	—

Uses.—(*a*) Tantalum is produced in the form of bars, sheet, and wire. It was formerly used as a lamp filament, and to a limited extent for surgical and dental instruments. The metal resists the action of all acids except hydrofluoric, and is therefore used in the form of dishes for laboratory work, especially for use with aqua regia. Its chief limitation is, that it cannot be heated in contact with any gases (especially hydrogen or nitrogen) above 300° C., owing to the readiness with which it combines with them to form brittle compounds; it can be worked cold, but all annealing must be done in a high vacuum. On its gas-absorbing faculty is based its use as a "getter" for removing the last traces of gas from vacuum tubes. Another important use of the metal is as one of the electrodes in rectifiers for converting alternating to direct currents.

[1] Chapter by W. R. Schoeller, Ph.D., Metallurgical Chemist, London, England.

It has been proposed to add tantalum to alloys of metals of the iron group in order to increase their resistance to attack by acids, or to act as a scavenger for nitrogen..

(b) Within the years 1933–1935 columbium became of practical interest * The properties are very similar to those of tantalum, and it will be used for substantially the same purposes.

DETECTION IN MINERALS

Definitions.—The term "earth acid" (or "earth acids"), as used in this chapter, denotes only tantalic or columbic acid, or the mixed tantalic and columbic acids. It is not applied to tungstic or titanic acid, or oxide mixtures containing these bodies. The term "mixed pentoxides" is used to denote $(Ta, Cb)_2O_5$.

The finely powdered mineral is digested at 60° C. with strong hydrochloric acid; nitric acid is added, and the liquid evaporated to dryness. The residue is moistened with hydrochloric acid, which is diluted with water; the solution is boiled and filtered. The washed residue is digested with warm dilute ammonia, which extracts tungstic acid, and the ammoniacal solution filtered. The residue contains the tantalum and columbium, if present.

Schoeller's Test.—The residue is ignited in a silica crucible, and fused with potassium bisulfate; the fusion product is re-fused with a few drops of strong sulfuric acid at low temperature, and dissolved in a hot 20% solution of tartaric acid. The solution, freed from siliceous insoluble by filtration, if necessary, is boiled for 5 to 10 minutes with one-quarter to one-third its bulk of strong hydrochloric acid. A white flocculent precipitate reveals the presence of earth acid. The reaction is specific and sensitive.[2]

The precipitate is collected and washed, after which it may be used for the separate identification of tantalum and columbium by one of the following three tests.

(1) **Marignac's Test** (does not detect small quantities of tantalum in presence of much columbium).—The washed precipitate is dissolved in a minimum of hydrofluoric acid, a saturated solution of potassium fluoride added, the solution evaporated to small bulk and allowed to cool slowly. A crystalline precipitate (potassium fluotantalate, K_2TaF_7, acicular rhombic prisms soluble in 200 parts of water) indicates tantalum. The columbium is in the filtrate, from which it separates on further evaporation as platy crystals of potassium fluoxycolumbate, $K_2CbOF_5 \cdot H_2O$, soluble in 12 parts of water.

* C. W. Balke, Ind. Eng. Chem., 27, 1166, 1935.

[2] Analyst, 54, 453, 1929.

(2) **Giles's Test**[3] (sensitive test for small amounts of columbium).—The washed precipitate is ignited and fused with potassium carbonate. The clear melt is cooled, dissolved in a little water, the solution treated with excess of phosphoric acid, and heated till clear. The hot liquid reduced with zinc dust strikes a brownish to inky-black color, depending on the amount of columbium present. Tantalum gives no coloration.

(3) **Powell and Schoeller's Test**[4] (the only wet test revealing small amounts of tantalum in presence of much columbium; applicable to the characterization of both elements when mixed in any proportions).—This is based on the fact that a solution of oxalotantalic acid gives a sulfur-yellow, one of oxalocolumbic acid a vermilion, precipitate with tannin.

The washed precipitate is ignited and fused with potassium bisulfate in a silica crucible, and the melt dissolved by boiling in 50 ml. of saturated ammonium oxalate solution. A few ml. are tested with hydrogen peroxide for titania, which should not constitute more than 2% of the oxides; otherwise the precipitate under examination must be purified. This is done by ignition, fusion with bisulfate, solution in 20% tartaric acid, and boiling with strong hydrochloric acid, exactly as before.

The oxalate solution substantially free from titanium is treated while boiling with 0.1 to 0.2 gm. of tannin in hot water, followed by 0.5 N ammonia drop by drop till a flocculent precipitate is formed. If this is pale to bright yellow, the presence of tantalum is proved; if orange to red, columbium is present, with tantalum either absent or present in more or less subordinate amount. In the latter case the precipitate, after being collected and washed, is rinsed back, boiled with 25 ml. of ammonium oxalate solution, and dissolved by the gradual addition of N sulfuric acid; when clear, the boiling solution is treated with 0.1 gm. of tannin and 0.5 N ammonia drop by drop until a flocculent precipitate is again obtained. This will now be yellow if the amount of tantalum present is not too small. If again orange, the precipitate should be filtered and the treatment repeated once more. For the detection of traces of tantalum, it is best to follow the directions for the quantitative separation, described below.

In presence of much tantalum, columbium is readily detected in the filtrate from the first yellow tannin precipitate; the solution is boiled and treated with more tannin and excess of ammonium acetate. An orange-red to vermilion precipitate indicates columbium.

[3] Chem. News, 95, 1, 1907.
[4] Analyst, 50, 494, 1925.

DETECTION IN MIXED OXIDES

Schoeller's Process.[5]—This test, which can also be applied to minerals, is especially useful for the detection of the earth acids in impure oxides, more particularly titania and zirconia, and oxide mixtures containing but little earth acid.

The mixed oxides (0.1 to 0.2 gm.) are fused with bisulfate; the melt is made to solidify in a thin layer on the sides of the crucible, and digested on the waterbath with the tannin reagent (a one per cent solution of tannin in 5% sulfuric acid). When the melt has become detached, it is transferred to a beaker with more of the reagent; the liquid is heated to boiling, then left on the waterbath till clear. Titania, zirconia, and any sulfate-forming metals go into solution. If no precipitate is left, tantalum and columbium are absent; if a buff to scarlet precipitate has deposited, it is collected, washed with dilute sulfuric acid, ignited, fused with bisulfate, and the melt dissolved in a hot, strong solution of tartaric acid. The boiling liquid is treated with about one-quarter its bulk of strong hydrochloric acid as before; a white flocculent precipitate proves the earth acids to be present.

Tungsten, if present, will remain with the earth acids in the precipitate. In such a case, the precipitate will be light to dark coffee-brown in color, and be converted by ignition into an oxide which is bright yellow while hot. For the detection of the earth acids in the ignited oxide, this is fused with potassium carbonate at high temperature, the melt dissolved in a minimum of hot caustic potash, and the solution gradually treated with solid sodium chloride till saturated; a white crystalline precipitate forms if earth acids are present.[6] The precipitate is decomposed by acids with separation of white, flocculent earth acids.

ESTIMATION

INTRODUCTORY REMARKS ON ANALYTICAL TECHNIQUE

Fusion with Bisulfate.—Materials containing tantalum and columbium are sometimes brought into solution by means of hydrofluoric acid, but more generally by fusion processes. Of these the most generally applicable is fusion with alkali bisulfate, the potassium salt being the more convenient except when rare earths are present. Transparent silica glass crucibles should

[5] Analyst, 54, 453, 1929.
[6] Schoeller and Jahn, Analyst, 51, 613, 1926.

be used for the fusion in preference to platinum. The finely powdered material is fused at as low a temperature as possible, till crystals of neutral potassium sulfate form at the surface of the fluid melt; the mass is then spread around the sides of the crucible, left to cool, and moistened with 0.5 to 1 ml. of strong sulfuric acid. The fusion is repeated at low temperature. Even when the attack is complete in the first fusion, another fusion with sulfuric acid, resulting in a fluid acid melt, should be made. With this technique the attack on the crucible is practically negligible, and silica, if present in the material under treatment, remains insoluble. In the analysis of minerals and ores, the silica crucible should be weighed before and after fusion; an allowance for silica can then be made if at all necessary.

Leaching the Bisulfate Melt.—This must be done in the crucible, at least to the point where the cake becomes detached from the sides and can be transferred to a beaker; hence the melt should not be allowed to solidify undisturbed as a thick cake at the bottom of the crucible. The solvents used are either ammonium oxalate or tartaric acid. The latter is added in form of a hot, 20 to 30% solution; the liquid is gently warmed on a waterbath, and solution assisted by frequent stirring with a short, thin glass rod. The liquid is transferred to a small beaker with hot water, filtered, and the washed residue ignited in the same silica crucible and again fused with a little bisulfate exactly as before. Extraction of the cake with tartaric acid (a smaller quantity) is repeated, and the extracts combined. The re-treatment of the residue is recommended for two reasons: (1) to make sure that the attack was complete; (2) because tantaliferous materials poor in, or free from, columbium occasionally give trouble during leaching, part of the tantalic acid being precipitated by hydrolysis. This fraction is rendered soluble in the second fusion and leaching.

If the operator should be unable to obtain a clear tartrate liquor (with columbiferous materials this difficulty does not occur), he need not start afresh. The turbid solution—and the filter paper, if filtration has been started—is evaporated with nitric and a restricted amount of sulfuric acid till the organic matter has been destroyed. The residual acid sulfate mass will dissolve to a clear liquid in tartaric acid solution.

Destruction of Tartaric (Citric) Acid, Tannin, and Filter Paper.—A brief description of this operation may not be out of place. A wet filter, containing a precipitate, dissolves when dropped into a few ml. of a strong sulfuric acid. For the destruction of the organic matter, the beaker is placed on a hot plate, when water is expelled and the mass blackens and foams. The beaker is now covered, and a few drops of strong nitric acid dropped on to the liquid from a tube inserted through the spout. The dark color is discharged with copious evolution of red fumes. All the organic matter is destroyed when the liquid, upon evaporation to fumes, remains colorless; if not, it is allowed to cool somewhat, and again treated with a little nitric acid, etc.

For the destruction of tartaric (citric) acid or tannin, the solution is evaporated with a few ml. of sulfuric acid until charring has set in. Repeated treatment with small quantities of nitric acid is then applied as described.

Filtration and Washing of Amorphous Precipitates.—Earth-acid precipitates are said to be difficult to filter and wash, but if properly precipitated they are as tractable as ferric hydroxide, which they resemble in regard to adsorption and other physical properties. The same remarks apply to tannin precipitates of

tantalum, columbium, titanium, zirconium, aluminum, etc. The latter are very voluminous, a property invaluable in micro-work, but undesirable for the treatment of substantial quantities of the elements. The inconvenience is largely overcome by filtration under gentle suction, which reduces the bulk to such an extent that the tannin complex formed by 0.1 gm. of titania can be collected on an 11 cm. filter. For filtrations at atmospheric pressure, a loose-textured paper is perfectly safe. The quickest way of effecting filtration is as follows: the clear supernatant liquid is poured off into a clean beaker and filtered; the beaker is rinsed and discarded. The precipitate is then intimately mixed with finely divided pulped filter fiber, and transferred to the filter. After draining, it is returned to the beaker, and thoroughly stirred up with wash-liquor. It is then collected on the filter and washed in the usual manner. The beaker in which the precipitation was carried out is cleaned with a little filter pulp, which is rubbed over the glass with a rubber-tipped glass rod. The wash-liquor should contain an electrolyte (e.g., the ammonium salt of a mineral acid), and a little tannin in the case of tannin precipitates. Stained beakers are cleaned with a boiling solution of oxalic acid in moderately strong hydrochloric acid.

Ignition of Precipitates.—The time-honored technique consists in igniting earth-acid precipitates in platinum crucibles at high temperature to constant weight, with addition of ammonium carbonate. The precipitate is then in the form of hard lumps difficult to free from sulfur trioxide, not easily attacked by bisulfate, and often discolored, due probably to reduction by diffusing burner gases. The precipitates should be mixed with filter fiber as directed above, and ignited (without previous drying) in porcelain crucibles. The ignition leaves the oxides as a soft, light powder. This is digested with hot, very dilute hydrochloric acid, which extracts sulfur trioxide and alkali. The solution is then made slightly ammoniacal, the precipitate collected on a small filter, strongly ignited in the same crucible, and weighed. It is next tested for impurities by fusion with bisulfate and solution of the cake in a solution of tartaric acid and ammonium oxalate. The liquor is transferred to a small beaker (not filtered), the crucible rinsed, and the solution treated with a small excess of ammonia and hydrogen sulfide water. The dark precipitate is allowed to flocculate by digestion at gentle heat, collected, well washed, ignited, and weighed as ($SiO_2+Fe_2O_3+CaO$). The weight is subtracted from that of the oxide previously obtained. Special precautions should be taken to employ the purest reagents free from glass splinters or gritty matter. This applies more particularly to the bisulfate.

Quarter-gram Analysis.—For the final separation of tantalum and columbium by fractional crystallization of the double fluorides, a quantity of 20 to 30 gms. of mineral was considered necessary. The introduction of tannin as a reagent in earth-acid analysis has made it possible to determine the major constituents in 0.25 gm. of mineral. There seems to be no advantage in working on a larger sample: on the contrary, the reactions described below tend to proceed more smoothly and furnish better separations with less labor when "quarter-gram analysis" is practiced.

PREPARATION OF THE SOLUTION

Tantalum and columbium are distinguished from other elements by the very small number of their stable water-soluble compounds, a fact which accounts for most of the difficulties encountered in earth-acid analysis. The fluorides are very stable, but their application precludes the employment of glassware. The earth acids and their minerals are attacked by fused potassium bifluoride, and more or less readily by hydrofluoric acid. The pure fluorides of tantalum and columbium are volatile, but their aqueous solutions hydrolyze upon evaporation, hence no volatilization loss occurs. The dry residue, if free from alkali fluoride, can be heated without loss. Nor is there any loss when a fluoride solution containing sulfuric acid is evaporated, and the sulfuric acid expelled by heating.

In the process hitherto most commonly employed for the assay of tantalite, the earth acids are not obtained in a soluble form at all prior to their separation from each other in fluoride solution: the bisulfate melt of the mineral is boiled with water or dilute sulfuric acid, the earth acids remaining insoluble; a purification of the impure precipitate by extraction with various reagents is then attempted.

The following water-soluble compounds of the earth acids are of interest in analytical work: (1) The *tartaric acid complexes*. The procedure for preparing them has already been described in the preceding Section (under "Leaching the Bisulfate Melt"), from which it appears that the tantalum complex has the greater tendency to dissociate. The ammoniacal are stabler than the acid tartrate solutions. Citric acid also forms soluble earth-acid complexes.

(2) The *oxalic acid complexes* are obtained, like the preceding, from a bisulfate melt of the earth acids: this is dissolved in a saturated hot solution of ammonium oxalate. Oxalocolumbic acid is much stabler than the tantalum compound, an observation applied in the separation of the two elements.

(3) The *per-acids* are obtained when a bisulfate melt of the earth acids is digested with a mixture of dilute sulfuric acid and hydrogen peroxide. Again the columbium compound is stabler than that of tantalum, which begins to decompose after some hours. The solution of the per-acids is colorless.

(4) The *potassium salts*. Fusion of the earth acids (or their minerals) with potassium carbonate or hydroxide yields the 4 : 3 (or "hexa") salts, $4K_2O \cdot 3(Ta, Cb)_2O_5$. These are soluble in water; the columbate is a fairly stable salt, but the tantalate dissociates more readily (especially in dilute solution), with precipitation of tantalic acid. The presence of potassium hydroxide increases the stability of the solution. If the solution of the potassium salts is saturated with sodium chloride by addition of solid salt, crystalline precipitates of the following composition are obtained:

$4Na_2O \cdot 3Ta_2O_5$, 4 : 3 sodium tantalate.

$7Na_2O \cdot 6Cb_2O_5$, 7 : 6 sodium columbate.

The soda in these precipitates can be titrated acidimetrically, which gives a measure of the earth acid combined with it. With mixed earth-acid salts, the values thus obtained are not sufficiently close for an accurate estimation of tantalum and columbium by the "indirect" method.

Treatment of Minerals.—It will be apparent from the preceding remarks that solution of earth-acid minerals may be brought about by (1) hydrofluoric acid, (2) alkali bisulfate, or (3) potassium hydroxide. Accordingly, these three types of procedure for obtaining a solution of the sample will be given. Since however the subsequent treatment of the solution varies with the mode of attack, the preparation of the solution will be described in each case as part of the process of analysis. (See below, under "Gravimetric Methods.")

SEPARATIONS

This Section describes the more recently published, improved methods for the separation of the earth acids from their more common mineral associates, namely: silica, tin, tungsten, iron, titanium, zirconium, thorium and rare earths.

From Silica.[7]—(*a*) The earth-acid mineral, or a mixture of oxides low in silica, is fused with bisulfate, and the fused product extracted with tartaric acid (or ammonium oxalate) solution, as described under "Introductory Remarks." The earth acids pass into the filtrate, whilst silica remains in the insoluble residue, which is treated as under (*b*) below.

(*b*) For the detection and determination of subordinate to minute amounts of earth acids in silica, the ignited and weighed oxide is treated by the usual process of evaporation with hydrofluoric and sulfuric acids in a platinum crucible. The residue (if any), left after expulsion of the sulfuric acid, is strongly ignited and weighed, silica being found by difference. The fixed residue is then fused with bisulfate, and the mass dissolved in tartaric acid solution, which is added to the main solution obtained under (*a*).

From Tin.[8]—(*a*) Small amounts of stannic oxide are separated from the earth acids, like silica, by fusion with bisulfate and leaching with tartaric acid solution: stannic oxide remains in the insoluble residue, but not wholly so. The liquid resulting from the leaching, and containing the suspended stannic oxide, is treated with hydrogen sulfide and a little filter pulp, and filtered. The precipitate is collected, cautiously ignited in the fusion crucible, and again submitted to bisulfate fusion followed by tartaric acid leaching and hydrogen sulfide treatment. The second mixed oxide and sulfide precipitate is ignited to SnO_2, and weighed.

The same procedure will separate the earth acids from silica and stannic oxide: the insoluble residue from the above double treatment is weighed as (SiO_2+SnO_2), which is treated with sulfuric and hydrofluoric acids.

(*b*) Small amounts of earth acid are detected and determined in tin oxide (cassiterite) by initial reduction of the fine powder in a stream of hydrogen at red heat. The reduced tin is dissolved in hydrochloric acid; the residue from the extraction is submitted to the process described under (*a*).

From Tungsten.—Tungstic acid follows the earth acids in their hydrolytic precipitation reactions, and its extraction from the hydrolysis precipitate by ammonia or ammonium sulfide is incomplete. Fusion of the mixed oxides with sodium carbonate and sulfur is likewise unsatisfactory. Two methods have

[7] Schoeller and Powell, Analyst, 53, 258, 1928.
[8] Schoeller and Webb, Analyst, 56, 795, 1931.

been found to give a satisfactory separation. The first is founded on the insolubility of sodium tantalate and columbate and the solubility of sodium tungstate in solutions of high sodium ion concentration.[9] (See *a*, *b*.) The second is based on the precipitation of the earth acids, together with any other earths that may be present (e.g., titania) by ammoniacal magnesium salt solution from a solution of the mixed potassium salts, potassium tungstate remaining dissolved.[10] (See *c*.)

(a) Small Amounts of Tungstic Acid from Much Earth Acid.—The mixed oxides are fused with 3 gms. of potassium carbonate in a platinum crucible. The mass is dissolved with less than 0.5 gm. of potassium hydroxide by digestion with hot water, the liquid transferred to a small beaker, and gradually saturated with solid sodium chloride. The crystalline precipitate, P^1, is collected next day, well washed with half-saturated sodium chloride solution, and reserved. The filtrate is neutralized with dilute hydrochloric acid against phenolphthalein, and heated on the waterbath. The returning color is discharged at intervals with dilute acid. The small amount of earth acid that had escaped precipitation thus flocculates after a few hours' digestion: the precipitate, P^2, is filtered off and washed as P^1. The filters containing P^1 and P^2 are returned to the last beaker, stirred to a pulp with hot water, and treated with a slight excess of hydrochloric acid (methyl orange); the precipitate, after digestion on the waterbath, is filtered off, washed with dilute ammonium nitrate solution, ignited strongly, and weighed as $(Ta, Cb)_2O_5$.

The filtrate from P^2, containing the small quantity of tungstate, is acidified to the bicarbonate stage against phenolphthalein, and a fresh solution of 0.5 gm. tannin added. Treatment with dilute acid is now continued till the solution is plainly acid; the liquid is then warmed, and treated with 10 ml. of 2.5% cinchonine hydrochloride solution; the solution is then left in the cold for 6 hours or overnight. The clear liquid is poured through a filter, the brown precipitate well mixed with pulp, transferred to the filter, and washed very thoroughly with ammonium chloride solution containing a little tannin. It is dried in a tared porcelain crucible, and ignited over a Bunsen burner to WO_3, which is weighed.

(b) Small Amounts of Earth Acid in Tungsten Trioxide.—One gm. is fused with 2 gms. of sodium hydroxide in a nickel crucible for a minute; when cold, the product is taken up in 10 ml. of hot half-saturated sodium chloride solution. After standing for some hours in the cold, the small precipitate is collected on a minute dense pad of filter pulp and washed with the same sodium chloride solution in portions of 1 ml. at a time till the washings are practically neutral to litmus. Pulp and precipitate are rinsed into a very small beaker, digested with a few drops of dilute hydrochloric acid, collected on a small filter, washed with ammonium nitrate solution, and ignited to $(Ta, Cb)_2O_5$.

(c) Separation of Tungsten from Columbium, Titanium, Tantalum, and Zirconium.—The mixed oxides are fused with potassium carbonate (4 gm.) in a platinum crucible; the fused mass is disintegrated with water by gentle boiling, any lumps being broken up with a glass rod. The hot solution (150–200 ml.) is stirred and treated drop by drop with 25 ml. of a solution containing 1 g. of magnesium sulfate, 2 g. of ammonium chloride, and a few drops of

[9] Schoeller and Jahn, Analyst, 52, 506, 1927.
[10] Powell, Schoeller, and Jahn, Analyst, 60, 506, 1935.

ammonia. After half an hour's digestion on a steam bath, the flocculent precipitate is collected and washed with 5% ammonium chloride solution. The tungsten in the filtrate is determined as under (*a*) by means of tannin and cinchonine, after addition of 10 g. of ammonium chloride.

The precipitate produced by the magnesium reagent, containing the whole of the earths, is returned to the beaker; the washed filter paper is ignited, and the ash added to the solution. The liquid (150 ml.) is treated with a slight excess of hydrochloric acid and allowed to stand on a hot plate for half an hour. An equal volume of saturated ammonium chloride solution is added, and the free acid is nearly neutralized to litmus with ammonia. The solution is boiled and treated with 2 g. of ammonium acetate and a fresh solution of tannin until the precipitate flocculates. It is allowed to settle, mixed with a little filter pulp, collected, washed with dilute ammonium chloride solution, and ignited.

From Iron.—(*a*) The tartaric acid solution of the elements is treated with hydrogen sulfide till the iron is reduced, then with ammonia in excess and ammonium chloride, and digested on a covered waterbath till the ferrous sulfide has deposited. The precipitate is filtered off, washed as usual, and the iron re-precipitated as ferric hydroxide and finally weighed as Fe_2O_3.

The filtrate from the ferrous sulfide is acidified with hydrochloric acid and boiled till hydrogen sulfide is expelled, treated with one gm. of tannin in fresh solution, and titrated with ammonia (1 : 1); a strip of litmus paper adhering to the side of the beaker with its lower extremity in the liquid acts as indicator. The liquid is then treated with 5 to 10 gms. each of ammonium acetate and chloride, and boiled. The flocculent earth acid-tannin complex is left to settle, collected under slight suction, and further treated as described under "Filtration of Amorphous Precipitates."[11] Cupferron may be used, instead of tannin, for the precipitation of the earth acids; the precipitant is added to the cold hydrochloric acid solution after removal of the hydrogen sulfide; it is treated just like other precipitates produced by cupferron.[12]

(*b*) If the quantity of earth acids in the tartrate solution is substantial, the liquid is first boiled with 30 ml. of strong hydrochloric acid, as described below under Separation from Titanium, Method *A*. The well-washed earth-acid precipitate, which is free from iron, is ignited and weighed. The filtrate contains a small fraction of non-precipitated earth acid, and the iron; it is treated exactly as specified under (*a*) above.

From Titanium.—A practical solution of this difficult problem has been reached after investigations by the writer occupying eight years.

Small amounts of titania in tantalic and columbic oxides may be determined colorimetrically. For this purpose, the oxide is fused with bisulfate, the melt dissolved in ammonium oxalate solution, and the cold solution treated with sulfuric acid and hydrogen peroxide. The color is matched against that obtained by adding standardized titanium solution to one containing the same quantities of bisulfate, oxalate, acid, and peroxide as the solution to be tested.

In two respects, titania on the one hand and the earth acids on the other show differences in behavior which persist when the elements occur together in solution: (1) the earth acids do not, whilst titania does, form a soluble sulfate,

[11] Schoeller and Webb, Analyst, 54, 709, 1929.
[12] Pied, Compt. rend., 179, 897, 1924.

chloride, and nitrate (see Methods *A* and *B*); and (2) the earth acids do not, whilst titania does, form a soluble salicylic acid complex (see Method *C*).

Method A. Tartaric Hydrolysis.[13]—This process effects a rapid separation giving serviceable results provided the quantity of mixed oxides operated upon is below 0.05 gm. At the same time the earth acids are identified with certainty because the precipitation reaction is specific for tantalum and columbium. Therein lies the great value of the method.

The mixed oxides (about 0.05 gm.) are fused with 1 gm. (more or less) of bisulfate, and the product dissolved in a hot, strong solution of 2 gms. of tartaric acid. The resulting solution (100 ml.) is boiled and treated with 20 ml. of strong hydrochloric acid, and the boiling continued for 5 to 10 minutes. The white flocculent earth-acid precipitate is collected as described under *Introductory Remarks*, ignited, and weighed as $(Ta, Cb)_2O_5$. It contains a little titania, but on the other hand a little earth acid escapes precipitation, the two errors neutralizing each other.

Method B. Pyrosulfate-Tannin Method.[14]—This procedure is based on the fact that, upon extraction of the bisulfate melt of the mixed oxides with acid tannin solution, the earth acids remain as an insoluble residue (tannin complexes); titanium sulfate dissolves. It is a rapid and simple process for tracing and determining very small quantities of earth acid in titania.

The titanic oxide containing a few mgms. of earth acid is fused with bisulfate (2 to 3 gms.) in a silica crucible; the melt is spread around the sides of the crucible, and treated with the hot reagent (a 1 % solution of tannin in 5% sulfuric acid). When detached, the crucible contents are transferred to a 150 ml. beaker, and the crucible rinsed, with more of the reagent; the liquid is heated just to boiling, and left on the waterbath till the precipitate has settled. After several hours' standing in the cold or over night, the precipitate is collected, well washed with 2% sulfuric acid containing a little tannin, ignited, and weighed as $(Ta, Cb)_2O_5$.

The small amount of titania in the weighed precipitate may be determined colorimetrically; if a specific earth-acid test is desired, the precipitate is treated as under Method *A*.

Method C. Oxalate-Salicylate Method.[15]—This is the most accurate process, to be applied for the separation of substantial amounts of earth acid from titania.

The mixed oxides (0.2 to 0.3 gm.) are fused with bisulfate, and the product dissolved in a hot solution of 2.0 gms. of ammonium oxalate in an 800 ml. beaker. Addition of 5 gms. of sodium salicylate dissolved in water produces a yellow to orange solution. This is diluted to 250 ml., boiled, stirred, and gradually precipitated with a moderate excess of 20% calcium chloride solution. After a few minutes, the boiling-hot solution is filtered under slight suction, and the precipitate washed with hot 2% sodium salicylate solution till the washings are colorless.

Precipitate (P^1).—(1) This is returned to the precipitation vessel, and the filter well rinsed, with hot water; the paper is cleaned with 50 ml. of hydrochloric acid (1 : 1), ignited, and the ash added. The acid liquid is boiled and cautiously

[13] Schoeller and Jahn, Analyst, 54, 321, 1929.
[14] Schoeller, Analyst, 54, 455, 1929.
[15] Schoeller and Jahn, Analyst, 57, 75, 1932.

treated with excess of strong permanganate solution; the dark brown color is finally bleached with a little tannin solution. The liquid is now diluted to about 200 ml., boiled with a fresh solution of about 1 gm. of tannin for 5 minutes, and left to settle. The tannin precipitate, *TP*, containing the bulk of the earth acids, is collected, washed with ammonium chloride solution containing a little tannin, ignited in silica, and reserved.

Filtrate from P^1.—(2) The yellow titanium filtrate is boiled with 10 to 20 gms. of ammonium acetate and a solution of 2 to 3 gms. of tannin. The bulky red precipitate, *TiP*, is collected under suction, etc., as already described, and ignited in a silica crucible.

Minor Recoveries.—(3) (1) To complete the recovery of the oxides from solution, the hydrochloric acid filtrate from *TP* is neutralized with ammonia, treated with 5 ml. of acetic acid and 10 gms. of ammonium acetate, boiled down to 300 ml., and another 0.5 gm. of tannin added to the boiling solution. After settling for some hours in the cold, the small precipitate is collected, washed, and ignited.

(2) For the most accurate work the filtrate from *TiP* (which is found occasionally to contain a fraction of a mgm. of titania) is likewise re-worked: it is simply boiled down to about 250 ml., 0.5 gm. tannin being added towards the end. After standing some time in the cold or over night, the small precipitate is collected, washed, and ignited.

The two recovery precipitates (1) and (2) are added to *TiP*.

Recovery of Earth Acids from Titania Fraction.—(4) The crude titania fraction (*TiP*a nd the two small recovery precipitates) is fused with bisulfate and treated according to Method *B*. This yields a filtrate containing the purified titanium fraction, and a residue consisting of the balance of the earth acids, which is ignited and added to *TP*. The united precipitate represents (Ta, Cb)$_2$O$_5$ containing a few mgms. of titania. Now this amount, though ascertainable by colorimetry, may seriously interfere in the subsequent tannin separation of tantalum from columbium by discoloring the yellow tantalum precipitate.

Repetition of Treatment.—(5) It is therefore necessary to repeat the whole cycle of operations on the earth-acid fraction (each cycle occupies two days). The re-treatment leaves less than 0.001 gm. of titania in the final combined earth-acid precipitate, whilst the earth-acid result shows a negative error of the order of 0.001, or 0.002 gm. if the columbium content of the mixed oxides is very high.

Direct Determination of the Titania.—(6) The titania may be taken by difference. If a direct determination is desired, the combined filtrates from the first and second pyrosulfate-tannin treatments are diluted, nearly neutralized with ammonia, boiled, and treated with excess of ammonium acetate and nitrate. The precipitate is collected under suction, etc., as before. The ignited earth-acid and titania precipitates should be leached and tested for purity as explained under *Introductory Remarks*.

From Zirconium and Hafnium.—Fusion of the mixed oxides with bisulfate and boiling of the solution of the melt with water to hydrolyze the earth acids always results in a precipitate contaminated with zirconia.[16] An accurate separation is achieved by the following combination method.[17]

[16] Schoeller and Waterhouse, Analyst, 53, 467, 1928.
[17] Schoeller and Waterhouse, Analyst, 53, 515, 1928.

(a) **Small Amounts of Earth Acid from Much Zirconia.**—The mixed oxides are fused with bisulfate, the melt dissolved in ammonium oxalate solution, and the liquid boiled with a fresh solution of 0.2 gm. tannin. Ammonia (1 : 1) is now added to the boiling liquid during agitation: the precipitate which forms is at first yellow to orange, but as the slow addition of ammonia is continued a dirty-white precipitate indicates incipient zirconia precipitation. The precipitate is left to settle in a warm place, collected, washed, ignited in the fusion crucible, and again fused with bisulfate. The oxalate solution of the melt (less than 50 ml.) is boiled and treated with dilute ammonia until a faint cloudiness results; this is at once removed with a minimum of dilute hydrochloric acid. A few gms. of ammonium chloride are added, followed by a fresh 1% tannin solution added drop by drop until the colored precipitate flocculates, leaving the liquid clear on digestion. The precipitate is collected, washed, ignited, and weighed as $(Ta, Cb)_2O_5$.

If desired, the zirconia (*plus* hafnia) in the combined filtrates is estimated by hydrolysis with sodium thiosulfate, after destruction of the tannin and oxalic acid by fuming with nitric and sulfuric acids.

(b) **Large Amounts of Earth Acid from Zirconia.**—As the tannin precipitates are bulky, the following method is more convenient for large amounts of earth acid. The mixed oxides are fused with potassium carbonate, the product dissolved in the platinum crucible in hot water along with 0.5 gm. of potassium hydroxide. The liquid is transferred to a small beaker, well stirred with filter pulp, and filtered; if cloudy, the filtrate will clear by being poured once more through the same paper. The residue is well washed with 2% potassium carbonate solution, returned to the beaker, and the filter pulped with water. The mixture is acidified with dilute hydrochloric acid, made ammoniacal, collected, washed with dilute ammonium nitrate solution, and ignited in silica. It contains all the zirconia and a little earth acid, and is treated according to (*a*).

The alkaline filtrate containing the major fraction of the earth acids is acidified with dilute hydrochloric acid and boiled with a faint excess of ammonia. The precipitate is mixed with filter pulp, collected, washed with dilute ammonium nitrate solution, ignited, digested with hot acidulated water, again collected, ignited strongly, and weighed.

From Thoria and Rare Earths.—(*a*) Small amounts of thoria and rare earths are separated from large amounts of earth acid by tartaric hydrolysis,[18] as for the separation of the earth acids from iron, *b* (*supra*). The hydrolysis precipitate is free from rare earths, but may contain 1 to 2 mg. of thoria if that earth is present in appreciable quantity; in this case the precipitate should be ignited, fused with bisulfate, the melt dissolved in tartaric acid, and the precipitation repeated.

The filtrate or combined filtrate is made alkaline with strong ammonia, boiled, and treated with 1 g. of tannin and 5 g. of ammonium acetate, which precipitates the thoria and rare earths together with the minor earth-acid fraction. The precipitate is collected, washed with ammonium chloride solution, ignited, fused with bisulfate, and the melt is extracted with 5% oxalic acid solution.[19] The oxalates of thorium and the rare earths remain insoluble, the earth acids go into solution.

[18] Schoeller and Waterhouse, Analyst, 60, 288, 1935.
[19] Pied, loc. cit.

(*b*) In J. Lawrence Smith's method, the rare earths and thoria are separated as insoluble fluorides (see below, under Hydrofluoric Acid Method).

GRAVIMETRIC METHODS

A. Hydrofluoric Acid Method (J. L. Smith).—This is most suitable for minerals containing rare earths, such as samarskite, but not for tantalite (columbite).

The finely crushed mineral (0.25 to 0.5 gm.) is weighed into a platinum dish or crucible, stirred with a few drops of water, and treated with 5 to 10 ml. of hydrofluoric acid. Solution is assisted by warming and stirring with a platinum rod. If necessary, the crucible is heated on the waterbath, and fresh portions of acid added if evaporation has proceeded too far. When solution is complete, the acid is diluted with about 10 volumes of water; after standing over night the solution is filtered (rubber funnel) into a platinum dish; the residue (which may contain thorium, rare-earth, alkaline-earth, lead, and uranous fluorides) is well washed with 5% hydrofluoric acid. The filtrate and washings, containing the earth acids, titanium, tungsten, tin, and common metals, are evaporated with 15 ml. of sulfuric acid (1 : 1) until it fumes freely. It is left to cool, the sides of the dish are rinsed down with water, and the fuming is repeated so that about one-half of the acid is volatilized. When cold, the mass is treated with a warm, strong solution of 3 gms. of tartaric acid, and the liquid digested on the waterbath; the clear solution is transferred to a beaker. From this point onwards, the estimation is carried on as from the second paragraph under *B* below.

B. Tartaric-Acid Method[20] **(for Tantalite and Columbite).**—The finely-powdered mineral (0.5 gm.) is fused with bisulfate, the melt re-fused with sulfuric acid, and the mass dissolved in tartaric acid solution, as detailed under Introductory Remarks.

The liquid is saturated with hydrogen sulfide, and the solution is filtered; the precipitate contains the tin (see Separation from Tin, *a*).

The filtrate, measuring or concentrated to about 150 ml., is boiled with 25 ml. of strong hydrochloric acid for 3 minutes. The white flocculent precipitate represents the major earth-acid fraction, P^1, which is collected, washed, ignited and treated by the magnesia method (see Separation from Tungsten, *c*) if tungsten is present.[21]

The minor earth-acid fraction is recovered as explained under Separation from Iron (*a*): the filtrate from P^1 is treated with hydrogen sulfide and made ammoniacal, the ferrous sulfide is filtered off, and the filtrate is precipitated

[20] Schoeller and Webb, Analyst, 59, 669, 1934.
[21] Schoeller and Waterhouse, Analyst, 61, 449, 1936.

with tannin after neutralization. The precipitate, P^2, consisting of the balance of the earth acids, is ignited and added to P^1.

The weight of (P^1+P^2) is that of the mixed pentoxides *plus* titania (and tungstic oxide, unless this has been eliminated by the magnesia method). These two constituents are very subordinate in high-grade ores, and in the technical determination of tantalum the tungsten can be neglected. The percentage of titania should always be determined by a separate test.

The mineral (0.1 gm.) is fused with bisulfate, and the melt is dissolved in ammonium oxalate solution; the liquid is acidified with sulfuric acid, treated with hydrogen peroxide, and its tint compared with that of a standard, prepared from the same quantities of reagents and a suitable amount of ferric sulfate solution, to which a titanium sulfate solution (0.0001 gm. TiO_2 per ml.) is added.

If the titania in the mineral is less than about 1%, a straight separation of tantalum from columbium is carried out (see *D*), a colorimetric titania determination being made in the final tantalic oxide precipitate.

If the titania content of the ore is more than about 1%, the precipitate (P^1+P^2) must be treated by the oxalate-salicylate method (see Separation from Titania, Method C) prior to the separation of tantalum from columbium. If the titania is below 2–3%, a single treatment by the oxalate-salicylate method suffices; with higher percentages, the double treatment described above must be carried out.

C. **Alkali Fusion Method.**[22]—For high-grade tantalite (not columbite or stibiotantalite). The finely-powdered mineral (0.5 gm.) is added to 3 gms. of previously fused potassium hydroxide in a nickel crucible. The covered crucible is gradually heated, and the fusion maintained at a red heat for about 20 minutes. In order to prevent creeping of the fused alkali, it is advisable to place the crucible in the closely-fitting hole of a square of asbestos board, so that the upper two-thirds of the crucible are kept comparatively cool.

When cold, the crucible and lid are immersed in dilute hydrochloric acid in a covered 800 ml. beaker; crucible and lid are cleaned and withdrawn. The solution, containing 20 ml. of strong hydrochloric acid in a bulk of about 100 ml., is boiled until the precipitate is pure white, then diluted to 200 ml. and again boiled for 15 minutes. The precipitate is left to settle, mixed with filter pulp, collected, washed with dilute hydrochloric acid till free from iron and nickel, ignited, and weighed as mixed pentoxides.

The writer finds[23] that Simpson's method answers quite well as a technical process, but not for the most accurate work; a few mgms. of earth acid are not precipitated. The bulk of the tin present becomes soluble, but 1 to 2 mgms. remain in the precipitate. This also contains the tungstic acid, and part of the silica. The latter is eliminated in the subsequent bisulfate fusion of the pentoxide precipitate and ammonium oxalate leaching of the melt, i.e., the first two steps in the separation of tantalum from columbium. (See *D*.)

The mineral may also be opened up by fusion with sodium peroxide instead of potassium hydroxide. In that case, the hydrochloric acid solution of the melt should be thoroughly boiled to destroy hydrogen peroxide; addition of sulfurous acid to the boiling liquid is recommended.

[22] Simpson, Chem. News, 99, 243, 1909.
[23] Analyst, 56, 795, 1931.

D. Separation and Gravimetric Estimation of Tantalum and Columbium.—The method here given [24] is applicable to mixtures of the two elements in any proportions, and suitable for micro-work. It is based on the fact that oxalotantalic acid is easily dissociated unless a certain amount of free oxalic acid is present: on neutralization with ammonia, tantalic acid is precipitated. Oxalocolumbic acid is much more stable; its dilute solution is not precipitated by ammonia. Russ [25] attempted a separation along these lines, but found that the presence of tantalic acid induced complete precipitation of the columbic acid. The addition of tannin makes a separation practicable; in slightly acid oxalate solution, it precipitates the yellow tantalum complex. The bright vermilion columbium complex is precipitated by excess of tannin from neutral solution. The difference is not sufficiently marked for a clean-cut separation in one operation, so the procedure is one of fractionation. The color of the tantalum precipitate is the indicator for its freedom from columbium; a small admixture of the latter imparts a more or less pronounced orange tint to the otherwise pure yellow tantalum compound. If columbium preponderates largely, a yellow precipitate is not obtained at first, but the orange to red precipitate yields a yellow one in the second or, if necessary, third treatment. If the tantalum is in large excess, the separation may be feasible without re-treatment. Titania interferes in the separation by discoloring the tantalum precipitate in the direction of buff or brownish-yellow rather than orange. The method works normally if the titania is less than one-eightieth of the tantalic oxide present; [26] a deduction is made for the titania in the final tantalum precipitate, after a colorimetric determination on about 0.02 gm.

The Separation.—The mixed oxides, containing less than 0.25 gm. of tantalic oxide, are fused with bisulfate and the product dissolved in a saturated, hot solution of ammonium oxalate (2 to 4 gms.). Any siliceous matter is filtered off; it may be advisable to re-treat it so as to make sure of the complete solution of the earth acids.

The filtrate (or combined filtrate) is boiled, treated with 10 ml. of tannin reagent (a fresh 2% solution), and stirred while being titrated with 0.5 N ammonia until a permanent strong turbidity results. More tannin reagent is now added according to the quantity of tantalic oxide present; the total amount required is:

For less than 0.03 gm. Ta_2O_5: 10 ml.
For 0.03 to 0.06 gm. Ta_2O_5: 15 to 20 ml.
For 0.06 to 0.12 gm. Ta_2O_5: 25 to 30 ml.
For 0.12 to 0.18 gm. Ta_2O_5: 35 to 40 ml.
For 0.18 to 0.25 gm. Ta_2O_5: 45 to 50 ml.

The reagent is added cautiously and the effect noted. If the precipitate is yellow at first, showing a transient orange admixture which disappears more slowly by stirring, the addition should be interrupted before permanent discoloration occurs. A strong solution of 5 gms. of ammonium chloride is now added, the solution boiled for a few minutes, and left to settle. The precipitate

[24] Powell and Schoeller, Analyst, 50, 485, 1925; Schoeller, *ibid.*, 57, 750, 1932.
[25] Z. anorg. Chem., 31, 42, 1902.
[26] Schoeller and Powell, Analyst, 53, 266, 1928.

is collected and washed with 2% ammonium chloride solution. It will be either orange to red (see *Procedure A*) or yellow (see *Procedure B*).

Procedure A.—The filtrate from the tannin precipitate is boiled, treated with 5 to 10 ml. of tannin reagent, and 0.5 N ammonia drop by drop till the precipitate flocculates. This is left to stand over night, collected, washed as before, and ignited together with the first precipitate. The product contains the whole of the tantalum; it is re-treated as the original mixed oxides as far as *Procedure A*; the secondary precipitate will now be yellow, and the fractionation is continued as under *Procedure B*. The second orange precipitate produced under *Procedure A* acts as a collector for any tantalum left in solution after the first precipitation.

If the re-treatment of the combined precipitates should still yield an orange precipitate, another repetition of *Procedure A* is necessary.

Procedure B.—The yellow precipitate is ignited and reserved. The filtrate is boiled, treated with a little more tannin, and further neutralized. If the resulting precipitate is again yellow, it is collected, washed, and ignited in the crucible containing the first tantalum fraction; but if orange, it is ignited, fused, etc., and another fractionation carried out. The operations are uniform throughout the course of the separation, and result in three products: (1) yellow precipitates are ignited and eliminated from the analysis as final products, being all transferred to the crucible serving for the ignition of the tantalum fractions. (2) Orange precipitates are re-treated, care being taken that the whole of the tantalum is precipitated, as explained under *Procedure A*. (3) Tantalum-free columbium filtrates are combined and evaporated. After a few repetitions, a yellow precipitate is no longer obtained, and the intermediate fraction (2) becomes negligible.

Determination of Tantalum.—The ignited oxide from the combined yellow precipitates is leached hot with acidulated water, which is made ammoniacal before filtration. The precipitate is strongly ignited and weighed as Ta_2O_5, which may contain a little silica, lime, and titania. It is therefore fused with bisulfate, dissolved in ammonium oxalate, and the slight precipitate collected after settling, washed, and ignited to (SiO_2+CaO). The oxalate filtrate is acidified with sulfuric acid for the colorimetric determination of titania.

Determination of Columbium.—This may be taken by difference; if a direct determination is desired, the combined filtrates from the tantalum fractions are concentrated and treated hot with a slight excess of ammonia. The brown precipitate is collected under suction, etc., as already described, and ignited, leached, again ignited, and weighed. The weight must be corrected for impurities; the solution (after bisulfate and oxalate treatment) is first tested for titania with a few drops of hydrogen peroxide, then treated with tartaric acid, ammonia, and ammonium sulfide. The weight of the ignited precipitate $(SiO_2+Fe_2O_3+CaO)$ and that of the titania are subtracted from the gross Cb_2O_5 weight.

VOLUMETRIC METHODS

In view of the exceptional difficulties attending the separate determination of tantalum and columbium, difficulties which became well nigh insurmountable in presence of a substantial proportion of titania, volumetric oxidation methods were proposed by several investigators for the determination of columbium, and also of the sum of columbium and titanium, in presence of tantalum. These methods will not be described here, for they suffer from a common defect, namely, variable or incomplete reduction, which finds expression in an empirical factor.[27] The factor varies with different operators using the same process, and even with one operator using the same procedure at different times or with different qualities of zinc. A simple explanation is, that acid solutions of tantalum and columbium are more or less hydrolyzed during or even before reduction, with formation of a colloidal phase which is not reduced. The same conditions apply here as in the case of tungstic acid, which cannot be reduced to an oxide of constant composition. The criterion for a reliable volumetric method is a stoichiometric factor indicating complete reduction of Cb_2O_5 to Cb_2O_3 (and of TiO_2 to Ti_2O_3). Even so, the difficulty still remains. Having determined the sum ($Cb_2O_5+TiO_2$) accurately, the next problem is the separate determination of columbium or titanium with tantalum present. If the amount of titania is at all substantial, it cannot be determined colorimetrically with sufficient accuracy. The writer is satisfied that the problem cannot be solved by volumetric methods, while the gravimetric methods described in this chapter have stood the test of practical application in scientific and commercial work.

[27] Schoeller and Waterhouse, Analyst, 49, 215, 1924.

COPPER[1]

Cu, *at.wt.* 63.57; *sp.gr.* 8.92$^{20°}$; *m.p.* 1083 (*in air* 1065); *b.p.* 2310; *oxides* Cu_2O *and* CuO

Copper is found in nature in native state and combined, principally as sulfide, oxide and carbonate; less commonly in antimonides, arsenates, phosphates, silicates and sulfates. Among the more common minerals are chalcopyrite, $CuFeS_2$; chalcocite, Cu_2S; bornite, Cu_5FeS_4; tetrahedrite, $Cu_8Sb_2S_7$; cuprite, Cu_2O; malachite, $CuCO_3 \cdot Cu(OH)_2$; azurite, $2CuCO_3 \cdot Cu(OH)_2$.

DETECTION

Copper is precipitated in an acid solution by H_2S gas, along with the other members of the hydrogen sulfide group. The insolubility of its sulfide in sodium sulfide is a means of separating copper from arsenic, antimony, and tin. The sulfide dissolves in nitric acid (separation from mercury) along with lead, bismuth, and cadmium. Lead is precipitated as $PbSO_4$ by sulfuric acid and bismuth as the hydroxide, $Bi(OH)_3$, upon adding ammonium hydroxide. Copper passes into the filtrate, coloring this solution blue,

$$Cu(OH)_2 \cdot 2NH_4OH \cdot (NH_4)_2SO_4.$$

Flame Test.—Substances containing copper (sulfides oxidized by roasting), when moistened with hydrochloric acid and heated on a platinum wire in the flame, give a blue color in the reducing flame and a green tinge to the oxidizing flame.

Wet Tests.—Nitric acid dissolves the metal or the oxides (sulfides should be roasted), forming a green or bluish-green solution. Ammonium hydroxide added to this solution will precipitate a pale blue compound, which dissolves in excess with the formation of a blue solution. (Nickel also gives a blue color.)

[1] We have records of the use of copper alloys as far back as 4500 B.C. The element was known to the Assyrians, Babylonians, Egyptians, Israelites, Phoenicians and Chinese over four thousand years ago. The extended use of copper today places it with iron and aluminum in commercial importance. Considerable attention has been given to analytical methods of copper determination in ores, minerals, alloys, pharmaceutical products, insecticides, and in minute amounts in substances, on account of its importance and the varied nature of the substances in which it is determined by the analytical chemist.

Hydrogen sulfide passed into a copper solution which is free of SO_2 or an oxidizing agent, but somewhat acid with a mineral acid, precipitates at once brownish-black CuS or Cu_2S (distinction from nickel, cobalt and zinc), which is difficulty soluble in conc. hot HCl (distinction from antimony), insoluble in fixed alkaline polysulfides (distinction from gold and platinum), soluble in alkaline cyanides (distinction from lead, bismuth, cadmium, mercury and silver), soluble in nitric acid (distinction from sulfide of mercury), with production of a bluish solution (distinction from all other metals except silver).

Potassium ferrocyanide precipitates from an acid or neutral solution of a cupric salt reddish-brown cupric ferrocyanide, which can be confused only with similarly colored precipitates from molybdenum or uranium solutions.

Cupric salts in halogen acid solution are reduced to colorless cuprous compounds by metallic copper, stannous chloride and sulfurous acid; and in alkaline solution are reduced by grape sugar, arsenious or sulfurous acids.

Delicate Test for Copper by p-Dimethylaminobenzylidene-rhodanine.[1]

Reagents.—Two per cent hydrazine sulfate; 0.02% rhodanine in alcohol.

Procedure.—To 10 ml. of the solution add a few drops hydrazine sulfate, sufficient 6 N ammonia to give 1 to 2 ml. in excess, 0.2 ml. of rhodanine and acidify, after five minutes' standing, with 30% acetic acid. The cuprous copper reacts even in the ammoniacal medium with the indicator; the color is reddish-violet (100 mg. of copper per liter) or orange-brown (10 mg. and less); sensitivity, 0.5 mg. of copper per liter. The colors are more pronounced after acidifying with acetic acid. Even a solution containing 0.3 mg. of copper per liter gives a distinct red-brown color; sensitivity, 0.1 to 0.2 mg. of copper per liter. The blank shows a yellow to brownish-yellow tinge. In order to reach the maximum sensitivity, it is necessary to let the ammoniacal solution stand for five minutes before adding the acetic acid. The reaction is so extremely sensitive that in all samples of distilled water in the laboratory, the presence of 0.2 to 0.4 mg. of copper per liter could be shown. In the experiments described in this paper, conductivity water or redistilled water from glass vessels was used as a solvent. Water thus obtained gave a negative test for copper. The reaction according to the above procedure is very suitable for the detection of copper in the presence of other cations (silver and mercury excepted). One part of copper in the presence of 2000 parts of lead, bismuth, cadmium, nickel, cobalt and manganese, respectively, could be detected easily. The precipitate formed in the presence of lead or bismuth does not interfere.

Traces of iron do not interfere. Larger amounts can be made harmless by acidifying the ammoniacal solution with phosphoric acid instead of acetic acid. The hydrous ferric oxide goes into solution as colorless complex ferric phosphate. A solution containing 1 mg. of copper and 100 mg. of ferric iron in a liter gave a distinct test for copper. It should be mentioned that the color of the cuprous compound of rhodanine is less stable in phosphoric acid than in acetic acid. It seems that the reaction according to the general procedure is very suitable for the detection of traces of copper in distilled and tap water. The copper content can be approximated by using solutions of known content for comparison.

Detection of Copper in Water.—S. G. Clarke and B. Jones published a note concerning a new and very sensitive reaction for copper. The solution, which must be free from chloride, is neutralized and rendered faintly acid (1 drop of

[1] I. M. Kolthoff, J. Am. Chem. Soc., 52, 2222, 1930.

dilute sulfuric acid in excess) and placed in a 100-ml. Nessler glass. One gram of ammonium persulfate is dissolved in the solution; 1 ml. of a saturated alcoholic solution of dimethylglyoxime, 0.5 ml. of 0.5% silver nitrate and 2% of a 10% aqueous solution of pyridine are added and the whole stirred. Copper gives a reddish-violet color. The reaction is quite specific and sensitive to 0.1 mg. of copper in a liter. Kolthoff has modified this method by substituting potassium periodate in place of persulfate, which permits the presence of chloride in small amounts.[3]

Procedure.—To 10 ml. of water add 0.2 to 0.3 ml. of 0.1% dimethylglyoxime and 1 ml. of saturated potassium periodate solution. Observe the color after three to five minutes' standing. A violet-red color shows the presence of copper; sensitivity: 0.1 mg. of copper in a liter (1 : 10^7).

NOTES.—(1) It makes no difference whether the dimethylglyoxime or the periodate is added first. In order to avoid confusion with nickel, it is advisable to add the dimethylglyoxime first. (2) The red-violet color develops gradually and attains a maximum sensitivity after about five minutes' standing. After long standing, the color fades. Still the procedure described can be applied for the colorimetric determination of traces of copper in distilled water if comparisons are made within fifteen minutes after addition of the reagents.

ESTIMATION

The determination of copper is required in the following substances: *In ores*[1] *of copper*, in which it occurs as native copper or combined as sulfide, oxide, carbonate, chloride, silicate and basic sulfate. In furnace slags, mattes, concentrates, blister copper, bottoms. The determination of copper is required in the analysis of alloys containing copper,[1] brass, bronze, etc. It is occasionally looked for as an undesirable impurity in food products. It is determined in salts of copper, in insecticides, germicides, etc.

Unless provision is made for its removal copper in part will precipitate with aluminum when ammonium hydroxide is added (pH less than 7), a part will pass into solution as the copper ammonium ion and will precipitate with magnesium as phosphate.

Copper is effectively separated in acid solution as CuS by H_2S (pH less than 1). The acidity for precipitation is 6 ml. of concentrated HCl per 100 ml. of water, saturating with H_2S, then diluting with an equal volume of water and again saturating with H_2S. With pH values approaching 2 to 3 zinc is apt to precipitate with copper.

Copper minerals and ores are best decomposed with acids, starting with HCl to act on the oxides and following up with HNO_3. The residue contains but

[3] J. Am. Chem. Soc., 52, 2222, 1930.

little copper; this may be decomposed with HF and H_2SO_4 or by fusion according to standard procedures.

PREPARATION AND SOLUTION OF THE SAMPLE

Hydrochloric and sulfuric acids are effective in dissolving metallic copper only in presence of an oxidizing agent; nitric acid is the most active solvent. The oxides of copper may be dissolved in hydrochloric or sulfuric acid, but nitric acid is commonly used. Some refractory furnace products are with most certainty decomposed by treatment with hydrofluoric and fuming sulfuric acids followed by a bisulfate fusion.

Ores.—If the ore consists practically of a single mineral, the fineness of the sample need not exceed 80 mesh. If the ore is a mixture of minerals, lean and rich in copper, the laboratory sample should pass a 120-mesh sieve.

Metallic particles or masses are separated at some stage in the process of sampling and made into a separate sample. If the metallic portion is a small percentage of the total sample and consists of particles, the copper value of which is known to vary by a few per cent, no attempt is made to refine the sample of such, but a large portion, 10–100 grams, is taken for analysis and the copper determined in an aliquot part of the solution. If the metallic masses are a large percentage of the sample, large of size, or consisting of particles differing widely in copper content, a weighed amount of 1 to 50 lbs. is melted in a graphite crucible, with addition of suitable fluxes, such as powdered silica or lime, if necessary. Separate samples are made of the weighed products of the fusion and the copper content of the material before melting calculated from their analyses. The amount of sample taken for assay depends upon the richness of the ore, homogeneity of the material and the commercial importance of the determination. As a rule in the assay for purchase and sale, a 1 gram test portion is taken of finely pulverized samples containing over 30% copper, 2 to 3 grams of 30% ores and 5 grams of ores containing less than 10% copper.

Sulfide Ores and Matte.—One to five grams of the sample are dissolved by adding 10–20 ml. dilute nitric acid (1.2 sp.gr.), or 10 ml. conc. nitric acid saturated with potassium chlorate, and allowing the mixture to stand in a warm place for about 15 minutes before applying heat. Decomposition is completed by evaporating to small volume in a casserole or Pyrex beaker and continuing to dryness after addition of 10 ml. hydrochloric acid, or by adding 5–10 ml. 50% sulfuric acid to the assay in a flask or tall beaker and heating to fumes. Continuing the first procedure, the residue is taken up by warming with 20 ml. 10% H_2SO_4, diluting, boiling and filtering the residue of silica, lead sulfate and silver chloride from the copper solution. Continuing the second procedure, the mass of anhydrous salts is dissolved with water, silver precipitated by just sufficient NaCl solution if the determination is to be by the electrolytic method, and the solution filtered after it has reached room temperature when the per cent of silver present is high.

Oxidized Ores with the exclusion of details relating to the oxidation of sulfur are brought into solution by the same method of treatment as sulfide ores.

NOTES.—The sulfur that appears upon adding acid to the ore, with proper precautions, should be yellow. If it is dark and opaque, the solution has been overheated,

and some of the ore has been occluded. It is advisable in this case to remove the globule of sulfur and oxidize it separately with bromine and nitric acid, then boil out the bromine and add the solution to the rest of the sample.

Sulfide ores may be treated according to the procedure recommended for iron pyrites in the chapter on Sulfur, the ore being decomposed with a mixture of bromine and carbon tetrachloride, 2 : 3, followed by nitric acid and then sulfuric acid.

Treatment of Matte Slag.—Only by quick quenching of the molten slag is decomposition of the sample by acids made possible, without preliminary treatment with hydrofluoric acid. As a rule lime slags are readily decomposed by mixed acids. Extremely acid and high iron slags are apt to be refractory and are decomposed with most certainty by treatment with hydrofluoric acid followed by fusion with potassium bisulfate.

The following scheme [4] of attack, which also can be applied to silicious ores, with skilful manipulation gives very satisfactory results:

One gram of the 100-mesh fine slag is placed in a 250-ml. beaker of Jena glass, moistened with water, mixed with 3 ml. of sulfuric acid (sp.gr. 1.54), and then, while the particles of the slag are in suspension through rotary movement of the beaker, 15 ml. hydrochloric acid are added. The silica is gelatinized in 2 or 3 minutes by heating the beaker over a free flame. One ml. nitric acid, followed by a few drops of hydrofluoric acid, is added, and the heating continued in a hood until the material is nearly dry, and then to strong sulfuric acid fumes on a hot plate. When cool, 4 ml. of sulfuric acid are added.

The remainder of the procedure depends upon the method that is to be followed in the determination of copper. If the electrolytic method is preferred, 3 ml. of nitric acid are added; the mass heated until solution is effected, the liquid diluted to 175 ml. with cold, distilled water, and copper plated out in 20–35 minutes, using a rotating anode and $2\frac{1}{2}$ amperes current.

If the iodide method is to be followed, without addition of other acid than sulfuric, the mass is again heated to fumes. When cooled, 25–30 ml. water and 5 ml. hydrochloric acid are added and the liquid boiled until clear. After addition of 40 ml. saturated solution of sodium acetate, $4\frac{1}{2}\%$ solution of sodium fluoride is added until the color of ferric acetate is discharged, and then an excess of 10 ml. When cold, titration is commenced, using a thiosulfate solution with a copper equivalent of 0.0005 g. per ml.

The following quick method has been systematically and satisfactorily checked for a long period by a hydrofluoric acid-bisulfate fusion method, by which copper, precipitated as a sulfide, is ignited, the oxide dissolved in nitric acid and copper determined by electrolysis.

Three grams of the 100-mesh fine sample are placed in an 800-ml. resistance beaker. The slag is spread over the bottom of the beaker, and while in motion 5 ml. of sulfuric acid are added rapidly to prevent the slag gathering into a mass. After addition of 40 ml. hydrochloric acid, the beaker is heated over a bare flame for about 3 minutes until the silica has gelatinized. To the hot solution nitric acid is added, drop by drop, until the liquid becomes dark brown. To the liquid, while in a state of agitation, 1–2 ml. hydrofluoric acid are added and the mixture boiled until the solution is complete. The liquid is diluted to 400 ml. and saturated with hydrogen sulfide and the precipitate

[4] White, Chemist-Analyst, July, 1912.

filtered and washed as usual. The copper sulfide is ignited in a silica crucible; the residue, if washing of the precipitate has been thorough, can be brushed into a 250-ml. beaker and dissolved with a few ml. of nitric acid. After boiling gently to expel nitrogen gases, the free acid is neutralized with ammonia, and the solution then acidified with a slight excess of acetic acid. The cold solution is titrated by the iodide method, using a thiosulfate solution having a copper equivalent of about 0.0005 g. per 1 ml.

Metals.—A casting of a copper alloy and even of refined copper is not homogeneous, and the zones of segregation of the constituents of the alloy (usually roughly parallel to the cooling surfaces) are the more sharply defined as the conditions which favor diffusion of the eutectic prevail; therefore, unless the casting be quite thin and quickly cooled, a satisfactorily representative sample of it cannot be obtained from a single drill hole. A single casting may be sampled by complete cross-sectional cuts by a suitable saw or by a series of drill holes located in such a manner as to amount substantially to one or more cross-sectional cuts. Steel is usually present as a contaminant of the drill or saw shavings from refined copper and the tougher alloys and should be removed by a magnet. Crude copper, such as blister or black copper, is sampled by drilling one hole in each piece of a definite fraction of the total pieces of the average lot. The position of the hole in successive pieces is changed to conform with a pattern or " templet " which will cover a quarter, or half, or the complete top surface of the average piece, the " templet " is divided into squares, preferably about 1 inch on a side, and in the centre of each square the ½-inch hole is drilled. The drillings are ground to pass a 20-mesh screen and the sample then withdrawn by means of a riffle sampler.

Sampling by splashing a molten stream with a wooden paddle and by slowly pouring the metal into water are methods frequently practiced. The size of the particles, the degree of homogeneity and the limit of accuracy of result required are factors which determine whether one or more grams of the sample should be taken for analysis.

Iron Ores and Iron Ore Briquettes.—A 5-gram sample of the finely divided material is fused in a large platinum dish with 40 grams of pure potassium bisulfate. If the ore is high in sulfur, it should be roasted by heating to redness in a silica or porcelain crucible before placing in the platinum dish and mixing with the bisulfate.

The cooled fusion is broken up into small pieces and placed in an 800-ml. beaker with clock-glass cover. Three hundred ml. of hot water and 25 ml. of conc. hydrochloric acid are added and the fusion is boiled until it passes into solution. If an appreciable residue remains, the solution is filtered, the residue fused with additional bisulfate, then dissolved in hot dilute acid and the filtrate added to the first solution. Silica and barium sulfate remain in the residue.

The solution is now reduced and copper precipitated according to directions given under " Separation of Copper by Precipitation in Metallic Form by a More Positive Element," aluminum powder being preferably used.

The precipitated copper is filtered free from iron and other commonly occurring impurities, then dissolved by pouring on the precipitated metal 30 ml. of hot dilute nitric acid, 1 : 1, followed by 10 ml. of bromine water and then 10 ml. of hot water. The filter paper is removed, ignited and the ash added to

the copper solution. The whole solution is now evaporated to small volume and determined, preferably, by the "Potassium Iodide" method as described under the volumetric procedures.

Steel, Cast Iron, and Alloy Steels.[5]—From 3 to 5 grams of steel, depending upon the amount of copper present, are dissolved in a mixture of 60 ml. of water and 7 ml. of sulfuric acid (sp.gr. 1.84) in a 250-ml. beaker. After all action has ceased, a strip of sheet aluminum, 1½ ins. square, bent so that it will stand upright in the beaker, is placed in the solution.

After boiling the solution for twenty to twenty-five minutes, which is sufficient to precipitate all of the copper in the sample, the beaker is removed from the heat and the cover and the sides washed down with cold water. The liquid is decanted through an 11-cm. filter, the precipitate washed three times with water, then placed with the filter in a 100-ml. beaker, and 8 ml. of concentrated nitric acid and 15 ml. of water are poured over the aluminum and the solution heated to boiling. This hot solution is poured over the precipitate and filter in the 100-ml. beaker, and boiled until the paper becomes a fine pulp, only a few minutes being required. The solution is filtered, the residue washed several times with hot water and copper determined in the filtrate by the electrolytic or iodide method.

SEPARATIONS

Separation of Copper as Cuprous Thiocyanate.—Isolation of copper from solutions containing iron, nickel, cobalt, zinc, cadmium, arsenic, antimony and tin may be accomplished by this method. When much arsenic is present, precipitation should be from a solution in which hydrochloric is the only free strong acid. Unless previously removed from the solution, lead, mercury, tellurium and the precious metals will contaminate the precipitate. Selenium may be a contaminant when present in considerable quantity, sometimes when the only free acid is sulfuric, always when hydrochloric acid is present.

Cuprous thiocyanate, besides being the medium of separation of copper from interfering elements preliminary to its determination by the standard electrolytic, iodide or cyanide method, is the basis of a number of other more or less useful gravimetric and volumetric methods of determining copper. The details of the procedure of procuring the precipitate are given under the gravimetric methods that follow.[6]

Electrolytic Separation of Copper.—Details of this separation are given under the gravimetric methods. The solution must be free from As, Sb, Sn, Mo, Au, Pt, Ag, Hg, Bi, Se, Te.

Separation of Copper by Precipitation in Metallic Form by a More Positive Element.—Details of this separation are given under the gravimetric methods.

Separation of Copper from Members of the Ammonium Sulfide and Subsequent Groups by Precipitation as Copper Sulfide in Acid Solution.—The solution containing free hydrochloric or sulfuric acid is saturated with H_2S gas, the precipitated copper sulfide (together with the members of the group) is filtered and washed, first with water containing H_2S and finally with a little

[5] W. B. Price, J. Ind. Eng. Chem., 6, 170, 1914.
[6] N. B. Demorest's method, J. Ind. Eng. Chem., 5, 216, 1913.

pure water. The residue is dissolved in nitric acid and the resulting solution examined for copper, separating it from members of its group.

Removal of Silver.—This element is precipitated as the insoluble chloride, $AgCl$, by addition of hydrochloric acid, and may be removed by filtration, copper passing into the filtrate.

Removal of Bismuth.—Upon adding ammonium hydroxide to a solution containing copper and bismuth the latter is precipitated as $Bi(OH)_3$ and may be removed by filtration. Copper passes into the filtrate as the double ammonium salt. Ammonium carbonate or potassium cyanide may be used instead of ammonium hydroxide.

Removal of Lead.—Lead is precipitated by sulfuric acid as $PbSO_4$ and may be removed by filtration, copper passing into the filtrate.

Removal of Mercury.—The sulfide of mercury remains undissolved when the precipitated sulfides are treated with dilute nitric acid, (1 part conc. HNO_3, 4 parts H_2O) copper sulfide dissolving readily.

Removal of Selenium and Tellurium.—Selenium can be eliminated from a copper solution by evaporating several times to dryness with hydrochloric acid. Saturation with SO_2 of a slightly acid sulfate of copper solution which contains about twice as much silver as selenium and boiling then to expel most of the gas will precipitate selenium and tellurium free of copper, also nearly all the silver. Precipitation of the remainder of the silver as $AgCl$ helps to retain the fine precipitate on the filter.

Removal of Arsenic, Antimony, Tin, Selenium and Tellurium.—Copper in minor quantity may be separated from these elements by passage of H_2S into the solution made slightly alkaline with sodium hydroxide, after addition of about a gram of tartaric acid if iron is present. Copper sulfide remains insoluble also when the mixed sulfides precipitated from an acid solution are treated with a hot mixture of sodium sulfide and hydroxide. These elements in minor quantity, whose presence in the electrolyte for copper determination is an objectionable impurity, are removed very satisfactorily by adding enough ferric iron to the solution to make the total iron present about twenty times that of the combined impurity, making ammoniacal and filtering after settling. Some copper is retained in the precipitate. Moderate amounts of arsenic may be eliminated as arsenious fluoride by the method employed to expel silica from an assay. Oxidizing agents must not be present.

In an alloy tin and antimony may be precipitated as oxides by evaporation of the solution of the alloy with concentrated nitric acid. A slight amount of copper may remain insoluble.

Separation from Cadmium.—The sulfides in a solution of dilute sulfuric acid, 1 : 4, are boiled and H_2S gas passed in for twenty minutes, the solution being kept at boiling temperature. Cadmium sulfide dissolves while copper sulfide remains unaffected. The solution is filtered hot, the air above the filter being displaced by CO_2 to prevent oxidation. Traces of cadmium are removed by repeating the operation. (Method by A. W. Hofmann.)

GRAVIMETRIC METHODS

METHODS OF ISOLATING COPPER

Separation of Copper as Cuprous Thiocyanate.—Isolation of copper from solutions containing iron, nickel, cobalt, zinc, cadmium, arsenic, antimony and tin may be accomplished by this method. When much arsenic is present, precipitation should be from a solution in which hydrochloric is the only free strong acid. Unless previously removed from the solution, lead, mercury, tellurium and the precious metals will contaminate the precipitate. Selenium may be a contaminant when present in considerable quantity, sometimes when the only free acid is sulfuric, always when hydrochloric acid is present.

Cuprous thiocyanate, besides being the medium of separation of copper from interfering elements preliminary to its determination by the standard electrolytic, iodide or cyanide method, is the basis of a number of other more or less useful gravimetric and volumetric methods of determining copper. The details of the procedure of procuring the precipitate vary to some extent with its object. Low grade copper ores may be conveniently determined by this method.[7]

Procedure.—To the cold, concentrated and very slightly acid copper solution (which must be free of any oxidizing agent) sulfur dioxide, gaseous or in solution, or a solution of an alkaline bisulfite or metabisulfite is added somewhat in excess of the quantity theoretically required to reduce all the copper and ferric iron present.

The liquid is cooled if hot, and then, with constant stirring, a solution of alkali thiocyanate of about normal strength is added until precipitation ceases. Reaction: $2CuSO_4 + 2KCNS + H_2SO_3 + H_2O = 2CuCNS + 2H_2SO_4 + K_2SO_4$. It is common practice to continue introduction of SO_2 throughout precipitation. The precipitate is allowed to stand until it is white and the liquid above it is clear. The presence of $FeSO_4$ accelerates conversion of cupric to cuprous thiocyanate when sulfuric is the only free acid. The precipitate is filtered off with the aid of reduced pressure through doubled filter papers of tight texture and washed with cold water until a washing is obtained which gives but very slight indication of thiocyanate when tested with a ferric salt.

The precipitate is inclined to float and creep with the capillary film of fluid, so precautions must be taken in its manipulation to avoid loss of copper on account of this characteristic.

The collected precipitate may now be treated in several ways which will produce a solution fit for the determination of copper by one of the standard methods. (*a*) The filter and precipitate are transferred to a porcelain or silica crucible which is very much larger than the volume of the wet precipitate, dried slowly in an oven or muffle and finally incinerated. Some operators made the final washing with 20% alcohol to facilitate drying or with a weak solution of an alkali nitrate to aid incineration. The residue is dissolved in the crucible with hot, concentrated nitric acid. (*b*) The point of the filter is

[7] With high grade ores or copper bullion a trace of copper (usually less than 0.0005 g. Cu) will pass into the filtrate when the copper precipitated amounts to 0.5 gram Cu. The loss with low grade copper ores is negligible.

punctured and the precipitate washed with as little water as possible into a flask or tall beaker. The filter is finally cleansed of adherent precipitate by washing with dilute nitric acid. The filter is dried, incinerated and dissolved separately or added to the main precipitate before its decomposition. Fifteen ml. conc. nitric acid are added for each gram or fraction of a gram of copper present and the covered beaker or funnel-closed flask allowed to stand in a warm place until the precipitate is dissolved, then boiled until solution is free of the nitrogen gases. It is the practice of some to add now 10–15 ml. of sulfuric acid and evaporate to fumes. Because evolution of gas during dissolution of the precipitate is profuse, care must be taken to expel the gas slowly to prevent boiling over.

Separation of Copper by Precipitation in Metallic Form by a More Positive Element.—Metallic aluminum or zinc is more commonly used in this procedure. A strip of pure aluminum or zinc, placed in the neutral or slightly acid solution, causes the complete deposition of copper. To obtain quick precipitation, a sheet of aluminum, 2.5 by 14 cm., is bent to raise the metal from the bottom of the beaker, placed in a covered 150-ml. beaker containing the copper solution, which should be not much over 75 ml. in volume and should hold about 10% of free H_2SO_4. Boil 7–10 minutes. The copper is removed mechanically from the displacing metal and dissolved in nitric acid and then determined by the Electrolytic or the Iodide Method.

A method of precipitation by means of powdered aluminum is recommended especially for separation of copper from large amounts of iron, iron ores and iron ore briquettes. The solution of the bisulfate fusion of the iron ore is heated until bubbles appear over the bottom of the containing beaker. Aluminum powder is now added in small portions at a time, in sufficient quantity to reduce the iron, the solution becoming colorless. The solution is now heated until the aluminum completely dissolves. Metallic copper is precipitated. It is advisable to add 25 ml. of water saturated with H_2S gas to precipitate traces of copper in solution. The solution is filtered while hot through a close thick filter, and washed six times, keeping the residue covered with water to prevent oxidation by air. The copper is now dissolved in hot dilute nitric acid, evaporated to small volume and determined by the procedure preferred. The potassium iodide method gives excellent results.

Occasionally the aluminum lies inert in the solution. If this occurs, two or three drops of hydrochloric acid (do not use much) will start a vigorous action and cause a rapid precipitation of metallic copper.

Separation of Bismuth from Copper.—Bismuth interferes with the electrolytic determination of copper, as it is deposited both on the anode and cathode, contaminating copper on the cathode. Its removal before the electrolysis of copper is necessary. It may best be separated as BiOBr, but its separation as oxynitrate is generally more convenient. The nitric acid solution of the two elements is almost neutralized with NH_4OH, then diluted to about 300 ml. and a slight excess of ammonium carbonate added and the solution boiled. The bismuth basic carbonate precipitate is filtered off and washed with hot water. It is advisable to dissolve in HNO_3 and reprecipitate to recover occluded copper. All the copper will be in solution.

DEPOSITION OF METALLIC COPPER BY ELECTROLYSIS

The electrolytic method of determining copper is the most accurate of the gravimetric methods. This deposition may conveniently be made from acid solutions containing free nitric or sulfuric acid, or from an ammoniacal solution.

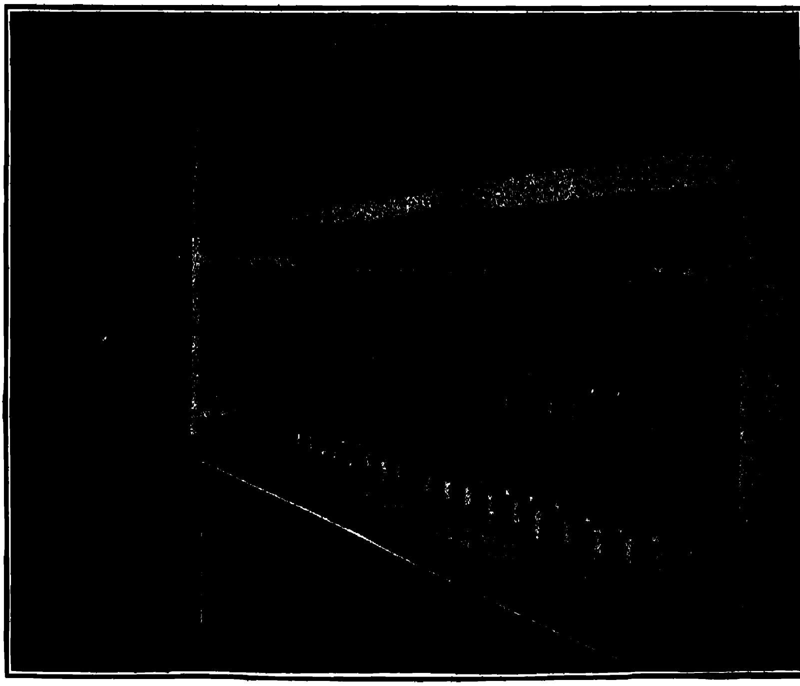


FIG. 39.—Terminal Case Showing Battery of Electrodes for Electrolytic Deposition of Copper.

The end sought by this method is to plate out all, except a trace, of the copper in the form of an evenly distributed, firmly adherent, very finely crystalline deposit, which is free from a weighable amount of impurity.

Five grams of copper may be deposited readily by the electrolytic method, while in other methods it is not advisable to determine more than 0.2 g. The solution must be free of Sb, As, Sn, Mo, Au, Pt, Ag, Hg, Bi, Se, Te and oxides of nitrogen. HCl causes a spongy deposit of copper.

In ores, mattes, alloys (from which lead has been removed as the sulfate by taking the solution to fumes with sulfuric acid), deposition by electrolysis, from a solution containing free sulfuric acid, is convenient. On the other hand, deposition from a nitric acid solution is advantageous under conditions where this reagent has been used as a solvent and evaporation with sulfuric acid is unnecessary. This is the case in the analysis of certain alloys and the determination of copper from which impurities have been largely removed. A chloride in an acid solution gives rise to a spongy deposit of copper, and endangers a solvent action on the anode and deposition of platinum on the cathode.

Conditions other than the presence of precipitable impurities which affect the character of the deposit are: quantity and concentration of copper, size and shape of electrodes, current density, uniformity of distribution of current to the cathode, volume, temperature and rate of circulation of the electrolyte, and concentration of oxidizing agents such as nitric acid and ferric salts. Inasmuch as the change of one condition limits or makes possible or necessary a modification of others, a large number of practicable combinations of conditions are possible. For discussion of these conditions reference is made to articles by Blasdale and Cruess, J. Am. Chem. Soc., 1264 (1910), and by Richards and Bisbee, J. Am. Chem. Soc., 530 (1904).

By the feature of rate of deposition, electrolytic methods may be classified as "slow" or "rapid." The slow methods, with 12 to 24 hour periods of electrolysis, are practiced when extreme accuracy is required, or when the distribution of laboratory labor and time allowed for completion of the assays permits their economical employment. The electrolyte is a solution of sulfate salts of the metals present, ammonium sulfate or nitrate, and a quantity of free nitric acid, which varies with the amount of copper and ferric salts present, and the current density employed. The oxidizing effect of nitric acid is intensified by the presence of ferric ions.[8] Electrolysis is carried out at room temperature, at current densities varying from ND/100, 0.15 to 0.5 ampere; and deposition on plain, corrugated, slit or perforated platinum cylinders from 0.75 to 2 in. diameter having 50 to 200 cm. depositing surface. A perforated cylinder permits freedom of circulation between the two surfaces of the electrode, the most even distribution of current density, and produces the most uniform coating of the foil. On account of the effect on the character of the deposit by oxygen lodging in regions of the cathode where the current density and circulation are least, the anode should be of such a form that all the gas liberated will be in the zone of maximum circulation. To procure uniform behavior under given conditions the size and shape of the electrolytic beaker should be such as to present the smallest practicable volume of electrolyte between the outer surface of the cylinder and the inside of the beaker. An unclosed seam or rivetted joint in a negative electrode will hold tenaciously salts which require extreme care to remove. It is probable that such recesses retain traces of the electrolyte underneath the coating of copper.

Rapid methods have a tendency to procure high results, resolution and mechanical loss through misting having been prevented. Deposition is hastened by increasing the rate of circulation and the current density. Circulation is promoted by the use of the gauze cathode,[9] by rotating either electrode,[10] or by placing the vessel, containing the solution and electrodes, in a field of electromagnetic force.[11] Quick deposition of a quality satisfactory for some classes of work is brought about by increase of current density upon an electrolyte heated to 50° to 80° C. In all the quick methods, the progress of electrolysis should be watched, and the cathode removed as soon as completion of deposition is de-

[8] Larison, Eng. and Mining J., 84, 442. Fairlie and Boone, Elect. and Met. Ind., 6, 58.

[9] Stoddard, J. Am. Chem. Soc., 31, 385 (1909). Price and Humphreys, J. Soc. Chem. Ind., 29, 307 (1910).

[10] Eng. and Mining J., 89, 89 (1910).

[11] Frary, J. Am. Chem. Soc., 29, 1592 (1907). Heath, J. Ind. Eng. Chem., 3, 76 (1911).

tected by the evolution of gas about its surface. The completion of action is ascertained with greater certainty by addition of water to the electrolyte and observing whether the newly exposed surface of the cathode remains bright. When the electrolyte is hot or has a high acid content, detachment of the cathode should be preceded by removal of the electrolyte and simultaneously washing the cathode without interruption of the current. A syphon may be employed, water being added as the liquid drains from the beaker until the acid is removed.

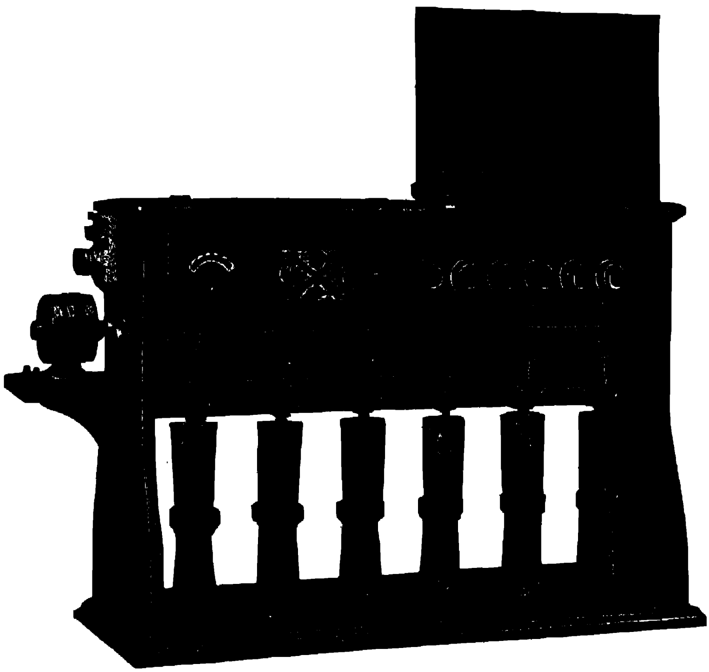


Fig. 40.

The illustration Fig. 40 shows a convenient form of cabinet for electrolytic determinations. The cabinet can be obtained from the Denver Fire Clay Co., Denver, or from Braun Corporation, Los Angeles. The anode may be rotated or left stationary as desired.

In the determination of copper in alloys, 0.5 g. alloy is dissolved in 10 ml. HNO_3 in a 250-ml. beaker, the solution diluted to 100 ml. is treated with 5 ml. H_2SO_4 and electrolyzed at $1\frac{1}{2}$–2 amperes. Do not use greater current. 0.2 g. Cu deposits readily in 1 hour with the rotating anode. Turn switch, after washing the deposit with water and alcohol, to " Off " position, otherwise the current will be broken through remaining units. Each unit has its own switch.

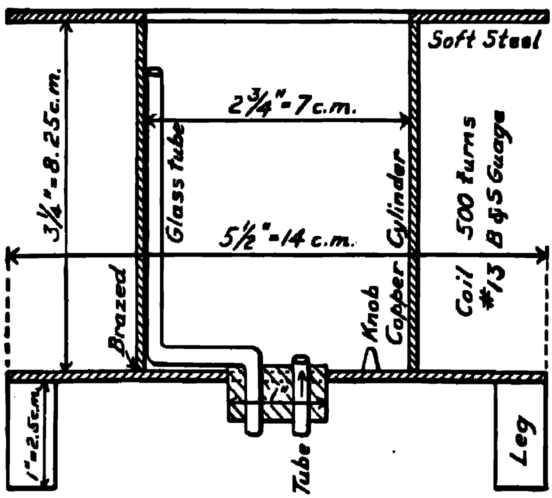
In determining copper in ores, iron is removed by precipitation with NH_4OH.(30% Fe carries down 0.3% Cu on 0.5 g. sample), lead is removed as sulfate and the filtrate electrolyzed for copper.

Copper is removed from the electrode by means of HNO_3.

RAPID METHODS

RAPID DEPOSITION OF COPPER—SOLENOID METHOD OF HEATH[13]

The solenoid is made by winding 500 turns of No. 13 B and S gauge magnet wire upon a copper cylinder $2\frac{3}{4}$ in. in diameter, $3\frac{1}{4}$ in. high, $\frac{3}{32}$ in. thickness of metal. The cylinder is brazed water tight at the bottom to a $5\frac{1}{2}$ in. disc of $\frac{3}{32}$ in. soft steel. In this disc is a 1-in. hole for the insertion of a rubber plug, through which glass tubes may be inserted for inlet and outlet of air or water to cool the electrolytic beaker. A steel disc of the same size as the bottom and with an opening to fit is brazed to the top of the cylinder. The solenoid thus made is suitable for a 300-ml. lipless beaker $4\frac{7}{8}$ in. high and $2\frac{1}{2}$ in. diameter. The solenoid coil may be in series in the electrolytic line or excited separately.



Solenoid for Rotation of the Electrolyte

FIG. 41.

The negative electrode is of gauze 40 meshes per linear inch, with a depositing surface of 100 sq. cm., and is slit to permit quick removal from the electrolyte.

Procedure.—Five grams of the thoroughly cleaned copper sample are dissolved in the covered electrolytic beaker on a steam plate with 40 ml. of stock acid solution composed of 7 parts (1.42 sp.gr.) nitric acid, 10 parts sulfuric acid (1.84 sp.gr.) and 25 parts by volume of water. The temperature during the solution is kept just below the boiling point, 50 ml. of the stock solution is used for copper containing 0.03 to 0.1% of arsenic, 60 ml. for material containing 0.11 to 0.5% arsenic. The electrolyte is diluted to 120 ml. A current of 4.5 amperes is used for the electrolysis and the same amount employed to excite the solenoid. During the deposition a double pair of watch glasses cover tightly the beaker until the color of the electrolyte fades out, when they are rinsed and

[13] Heath, J. Ind. Eng. Chem., 3, 76 (1911).

removed. Twenty minutes later and thereafter at 5 minute intervals, a test for completion of deposition is made by withdrawal of 1 ml. onto a porcelain tile and treating with a few drops of freshly prepared hydrogen sulfide water. This test will detect the presence of 0.000005 g. copper or more remaining in the solution. The determination is complete in two and a half hours. Extremely accurate results are obtained when the electrolyte is kept very cold by circulation of water about it and when the cathode is withdrawn within 5 minutes after completion of deposition.

In the assay of casting copper, in case the deposit is evidently impure, the cathode may be stripped by treatment with 50 ml. of the stock solvent and then replated under the conditions described.

NOTES.—The advantage of the solenoid over any mechanical device for the rotation of electrodes is due to the prevention of loss by spraying from the anode, as the beaker can be covered with a double pair of watch glasses.

Results range from 0.003 to 0.01% higher than the author's slow method of assay of refined copper, and are due to platinum from the anode, which is corroded by the influence of heat, nascent nitrous acid and high current.

Deposition from Nitric Acid Solution.—The solution should not contain over 2–3 ml. of free concentrated nitric acid. If more than this is present, the solution is evaporated to expel most of the acid, the remainder neutralized with ammonia and the requisite amount of nitric acid added. The solution is diluted to 100 ml., warmed to 50° or 60° C. and electrolyzed with a current of 1 ampere and 2–2.5 volts. Two hours are sufficient to deposit 0.3 gram copper. Since the hot acid acts vigorously on copper, it is necessary to wash out the acid from the beaker before breaking the current. (See method for copper in alloys, Vol. II, Chapter on Alloys.)

Deposition from an Ammoniacal Solution.—Ammonium hydroxide is added to the solution containing copper until the precipitate, first formed, dissolves. Twenty to twenty-five ml. of ammonium hydroxide (sp.gr. 0.96) are required for 0.5 gram copper or 30–35 ml. for 1 gram. Three to four grams of ammonium nitrate are added and the solution electrolyzed with a current of $ND/100=2$ amperes. The electrodes are washed, without breaking the current, until the ammonia and nitrate are removed.

Lead, bismuth, mercury, cadmium, zinc and nickel should be absent from the ammoniacal solution. Arsenic is not deposited. Unless a very pure platinum anode is used, platinum may contaminate the deposit appreciably. Jena or other brand of zinc borate resistance glass should not be used for the electrolytic beaker.

Rapid Deposition of Copper by the Rotating Anode.—The rapidity and completeness of the copper deposition, and to some extent its purity, depend on a continuous circulation and mixing of the solution. This may be accomplished by means of the rotating anode. The illustration shows a cabinet manufactured by the Braun Corporation that has proven to be compact and effective. Copper is deposited from a nitric acid solution with a current of 1.5 to 2.0 amperes.

SLOW METHODS

ELECTROLYTIC DETERMINATION OF COPPER IN BLISTER COPPER

The sample should be no coarser than 20 mesh. Because fine particles are comparatively poor in copper, extreme care must be taken in drawing the portion for analysis to preserve the ratio of the coarse to fine. To avoid sampling error, the laboratory sample should be sieved on 40 or 60 mesh, sieve; the " Coarse " and " Fine " assayed separately and the composite assay calculated according to proportion of each.

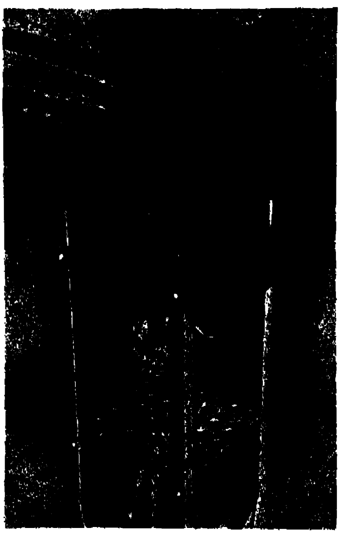


FIG. 42.—Riffle Sampler.

As an alternative a composite test may be run by weighing a proportionate amount of "Coarse" and "Fine." Some analysts draw a large portion by means of a riffle (Fig. 42) or similar sampling device and from its solution in a volumetric flask pipette an aliquot part equivalent to one or more grams.

By the small portion method insoluble matter must be removed by filtration. When the sample contains an insignificant quantity of insoluble matter, the practice is to deposit the silver with the copper and make a correction for its presence in accordance with the result of the silver assay of the sample.

By the large portion method, insoluble matter and silver, as silver chloride, are removed from the electrolyte by sedimentation in the volumetric flask.

Procedure. Small Portion Method.—The coarse and fine portions are quartered down to convenient amounts and from these a 5-gram composite weighed, which contains the coarse and fine portions in ratio of their percentage weights. The sample is placed in a 350-ml. tall-form beaker, without lip and with flaring rim. Fifty ml. of chlorine-free, stock acid solution (15 parts nitric and 5 parts sulfuric acids) are added, the beaker covered with a funnel (stem up), which just fits in the rim, and the mixture heated gently at first and finally to boiling. When the sample has dissolved, 5 ml. saturated solution of ammonium nitrate are added and the sample diluted to 200 ml. with water.

When the solution has cooled to room temperature the electrodes are introduced, the beaker covered with split watch glasses and electrolysis started with a current of .05 ampere and continued until the appearance of the foil indicates that the silver has deposited. The current is then raised to ND_{100} =.75 ampere and this continued for twenty to twenty-two hours, or until the appearance of gas about the negative electrode indicates that deposition of the copper is practically complete. For the unexperienced a simple method is to

add a little water to the electrolyte without breaking the current and after 15 minutes to observe whether any deposition of copper takes place on the freshly exposed surface. The watch glasses and electrode stems should be rinsed when the electrolysis has continued 15–16 hours.

Procedure. Large Portion Method.[11]—The sample is quartered by a riffle sampler (see Fig. 42) to an amount very close to 80 grams. This quantity is weighed and transferred by a paper chute into a 2000-ml. flask, which has been calibrated by the method of repeated delivery at constant temperature, of a 50 ml. overflow, dividing pipette (see Fig. 43). The liquid employed in calibrating is a copper solution of the same composition as that for which the flask is to be used. A cold mixture of 80 ml. sulfuric acid (sp.gr. 1.82) and 200 ml. nitric acid (1.42) with 500 ml. of water is added. A standard solution of sodium chloride is added in sufficient quantity to precipitate the silver, care being taken to add less than 20% excess. A bulbed condenser tube is placed in the neck before putting the flask on a hot plate.

The solution is gradually heated to boiling and when the solution is nearly complete, boiled gently for one hour. This generally completely dissolves the copper present. Residues of lead, tin, silver, or silica if present in appreciable amounts are separated at this point by filtration.

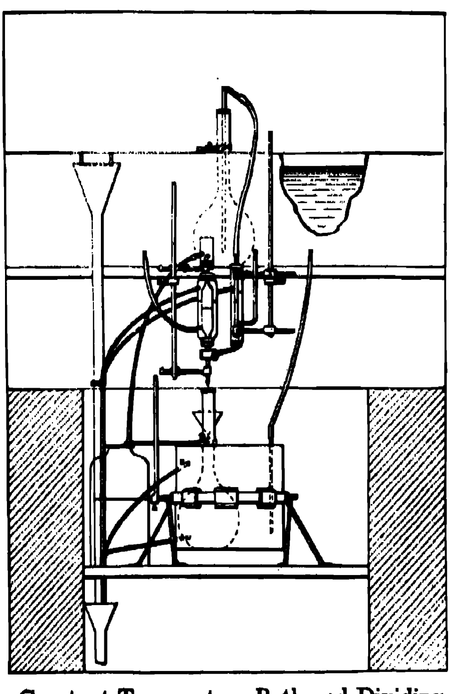


Fig. 43.—Constant Temperature Bath and Dividing Pipette.

When the solution in the flask has cooled for half an hour, water is added to a little above the 2000-ml. mark, giving the flask a rotary motion, during the addition, to mix the solution. The flask is placed in a large tank, Fig. 43,

[11] W. C. Ferguson, J. Ind. and Eng. Chem., 2, 187 (1910).

containing water and allowed to remain until it becomes of the same temperature as the water and very close to that of the room. The solution is then made exactly to the mark and allowed to settle, after thorough mixing, by placing the flask again in the water tank.

Electrolysis.—Portions equivalent to 2 grams of sample are measured out by means of a dividing pipette, with water-jacket through which the tank-water flows. The solution is run into glasses, hydrometer-jar in shape, with concave bottoms, height of glass $6\frac{1}{2}$ in., diameter $2\frac{1}{8}$ in., Fig. 44. Each portion is treated with 5 ml. of a saturated solution of ammonium nitrate and diluted to 125 ml. with water. (NH_4NO_3 or $(NH_4)_2SO_4$ delays deposition of As and Sb until electrolyte is freed from Cu.) The electrolyte, at this stage, contains about 3.7 ml. of nitric acid.

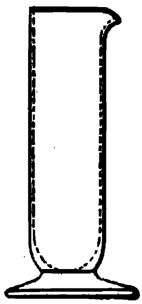


FIG. 44.–Hydrometer Jar for Electrolysis of Copper.

The copper is deposited by electrolysis, using a current of .33 ampere per 100 sq.cm., which is kept constant until deposition is complete, about twenty hours. It is advisable to begin the electrolysis in the evening, 5 P.M. The following morning, the inside of the jar, the rods of the electrodes, and the split watch-glasses which cover the jar are rinsed with a spray of water into the glass and the run continued for two or three hours. Each electrode is quickly detached from the binding posts, the cathode plunged into cold water, then successively into three jars of 95% alcohol, shaken free of adherent drops and dried by revolving rapidly over a Bunsen flame for a few seconds after ignition of the film of alcohol.

The weighing of electrode plus the deposit is made with as little delay as possible.

Determination of the Copper Remaining in the Electrolytes.—Since the exhausted electrolyte seldom contains over 0.01% copper, this residual copper can be closely estimated by observation of the depth of the sulfide precipitate. Should circumstances be such that the quantity is more than can be estimated by the appearance of the sulfide precipitate and a determination without rerun is necessary, the precipitate is filtered, incinerated, dissolved with a little hot HNO_3, made ammoniacal and, after settling, filtered through asbestos. The color of the solution is compared with a standard solution treated with the same amount of reagents as the sample, care being taken that similar conditions prevail when making comparison.

Notes and Precautions

Character of the Deposits.—The ideal deposit is of a salmon-pink color, silky in texture and luster, smooth and tightly adherent. A slightly spongy and coarsely crystalline deposit, although good in color and perfectly adherent, will invariably give high results. A loosely adherent deposit caused by either too rapid a deposition at the commencement or too low a current density at some period of the electrolysis usually shows a red tint and may give a high result on account of oxidation or a low result because of detachment of particles. A darkly shaded deposit indicates the presence of impurity in greater or less extent. If it is impossible to complete the electrolysis without this appearance the electrolyte should be purified. Impurities such as arsenic, antimony, bismuth, selenium and tellurium may occur in the blister copper.

A dark colored but perfectly adherent deposit is dissolved very slowly from the electrode, in a covered electrolytic jar, by gently heating for several hours with about 60–70

ml. of a solution containing 2 ml. sulfuric and 5 ml. nitric acids. When the solution is complete the temperature is raised to expel dissolved gases. Five ml. saturated ammonium nitrate solution is added and the electrolyte diluted to 125 ml. When cooled to room temperature, electrolysis is carried out under the same conditions as that of the first deposit and on the same electrode, if arsenic or antimony is the interfering impurity; on a fresh electrode if selenium or tellurium has been the contaminating element. The undeposited copper is determined colorimetrically in the mixture of the first and final electrolytes and added to the weight of the copper deposited.

If the sample contains a large percentage of arsenic or antimony, a portion representing 2 grams is drawn from a pipette into a Kjeldahl flask, 10 ml. of sulfuric acid added, and the liquid evaporated to fumes to expel nitric acid. From this solution cuprous thiocyanate is precipitated according to the method described on page 357. The funnel containing the filter is placed in a 500-ml. flask with long neck, the filter is punctured and the precipitate washed into the flask with the least quantity of water possible, the adherent precipitate is dissolved from the filter with warm dilute nitric acid, added cautiously to avoid violent evolution of gases from the dissolving precipitate in the flask. The washed filter is incinerated and the solution of its ash by nitric acid added to the electrolyte after completion of electrolysis. When solution of the precipitate is complete, the liquid is boiled to small volume, neutralized, and 5 ml. ammonium nitrate solution and 3 ml. excess free nitric acid added. The liquid is transferred to an electrolytic jar and electrolysis carried out in the manner already described.

The amounts of bismuth, arsenic, antimony, selenium or tellurium usually found in blister copper may be separated together with iron present by addition of ammonia to a pipetted portion. The filtered precipitate is purified of copper by solution with nitric acid and reprecipitation. The combined filtrates are neutralized, 3½ ml. of free nitric acid added and the solution electrolyzed under the conditions already described. The nitric acid solution of the incinerated filter, carrying the iron, etc., is added to the electrolyte, after electrolysis is complete, for determination as undeposited copper. The undeposited copper is determined colorimetrically by one of the procedures outlined later.

The deposited copper is never absolutely pure. The total impurities seldom exceed 0.03%. Ag from 0.000 to 0.18%; As from 0.000 to 0.003%; Sb from 0.000 to 0.004%; Se and Te from 0.001 to 0.027%; Bi from 0.000 to 0.0003%. Periodical complete analyses may be made and corrections applied to the analysis when exceedingly accurate percentages are required.

Too low a current density or excessive oxidizing power of the electrolyte may produce high results, due to the oxidation of the deposited copper. Too high a current density or a deficiency of oxidizing power in the electrolyte, by causing a deposition of impurities, will give high results.

The electrodes used by the Nichols Copper Co. are straight platinum wires for the positive ends and cylinders 1¾ in. long, 1 in. in diameter of 0.004 in. iridoplatinum foil, 11¼ sq. in. depositing surface, for the cathodes.

A uniform current is essential.

The nitric acid used should be free of iodic acid.

The presence of oxides of nitrogen gases, or a chloride in an acid solution, will cause a coarsely crystalline or brittle deposit, under conditions which in their absence would produce a good plating. The deposit moreover may contain platinum from the anode if the electrolyte contains a chloride salt.

Silver may be deposited with the copper and correction made for its presence from the result of a separate assay. Copper deposits in poor form, unless the silver be first plated out at a very low current density, about 0.03 Amp. ND_{100}.

Solid matter, unless removed, will contaminate the deposit mechanically.

Arsenic, antimony, selenium or tellurium has an influence on the physical character of the deposit which may affect the copper result beyond the sum of such impurities deposited.

Whether impurities are deposited or not, appreciably high results are obtained by continuing electrolysis for some time after the electrolyte has become impoverished of copper.

Overheating of the copper deposit, in the process of ignition of the alcohol clinging to the cathode, will cause oxidation of the copper. As much as possible of the alcohol must be shaken off before passing the electrode rapidly through the flame. It is advis-

able to weigh the copper shortly after deposition, as prolonged contact with air is undesirable, if extreme accuracy is desired.

The copper deposits may be removed by plunging the electrode, for a few moments, in hot nitric acid. After washing with water, the electrode is ignited to a cherry-red in a direct colorless flame. The ignition removes any grease, which would be objectionable, that may contaminate the platinum. Alcohol frequently contains oily matter which will cling to the electrode in spite of the rapid ignition for drying the deposit.

Other Methods.—The application of organic reagents is discussed in the chapter on Reagents, Section IV.

VOLUMETRIC METHODS FOR THE DETERMINATION OF COPPER

POTASSIUM IODIDE METHOD

The procedure depends upon the fact that cupric salts when treated with potassium iodide liberate iodine, the cuprous iodide formed being insoluble in dilute acetic acid, soluble in excess of potassium iodide.

Reactions.—$2CuSO_4+4KI=Cu_2I_2+2K_2SO_4+I_2$,

or $2Cu(C_2H_3O_2)_2+4KI=Cu_2I_2+4KC_2H_3O_2+I_2$.

The liberated iodine is titrated with standard thiosulfate.

$$2Na_2S_2O_3+I_2=Na_2S_4O_6+2NaI.$$

The method is of good accuracy.[13a] Only a few elements interfere, such as selenium, trivalent arsenic, antimony, iron and hexavalent molybdenum. Lead, mercury and silver increase the consumption of potassium iodide, but otherwise interfere only because of the color of their iodides. No free iodine is consumed by these.

The solution should not contain an excessive amount of ammonium acetate. If bromine is used to assist in oxidation free bromine should be completely expelled before neutralization with ammonia. The method outlined is a modification of the procedure recommended by A. H. Low, and if it is carefully conducted,[14] the end-point is sharp, without recurring color, as results from careless manipulation.

Standard Thiosulfate.—0.1 N Solution ($Na_2S_2O_3\cdot5H_2O$, 24.82 grams per liter).

Standardization with Metallic Copper.—Dissolve 0.1 gram of pure copper (electrolytic) in 5 ml. of nitric acid and boil gently to expel brown fumes. Dilute to about 20 ml. and add ammonia drop by drop until the precipitate that forms just dissolves and the solution is a deep blue color and again boil

[13a] Good to ±0.2% of the sample for materials high in copper (i.e. containing 80–95% Cu).

[14] Certain details developed by W. W. Scott, assisted by S. M. Alldredge, have made it possible to obtain a sharp, stable end-point.

until the odor of ammonia is faint. Neutralize with glacial acetic acid added drop by drop until the precipitate that forms with the acid dissolves and add five to six drops in excess. Again bring to boiling. Thoroughly cool and add solid potassium iodide in just sufficient amount to redissolve the copper iodide precipitate that forms. Titrate with the standard thiosulfate, adding the reagent until the brownish-red color fades to a light yellow color. Add starch indicator and complete the titration, adding the thiosulfate very cautiously, stirring vigorously, until a drop produces a colorless solution.

Divide the weight of copper taken by the ml. of reagent required to obtain the value of the reagent in terms of copper.

One ml. of 0.1 N solution is equivalent to 0.006357 g. Cu.

Standardization with Permanganate.—The reagent may be standardized against N/10 potassium permanganate or a permanganate solution whose iron equivalent is known. To about 40 ml. of the N/10 permanganate solution add 6 ml. of the potassium iodide (50%) reagent and titrate the liberated iodine in presence of acetic acid exactly as is described above. One ml. of N/10 permanganate should equal 1 ml. of the N/10 thiosulfate. Establish its normality by converting the permanganate to exact ml. in normality equivalent and dividing the ml. by the ml. of thiosulfate required. If preferred, multiply the iron equivalent by $\frac{63.57}{55.84} = 1.139$ to get the copper equivalent.

PROCEDURE FOR COPPER IN ORES

Solution of the Sample.—Weigh 0.5 gram of the powdered ore (if a N/10 thiosulfate reagent is to be used, the factor weight 0.636 gram of ore is convenient so that 1 ml. of the reagent is equivalent to 1% Cu). Dissolve in 10 ml. hydrochloric acid and 5 ml. nitric, heating gently to effect solution, adding more of the acids if necessary. Add 10 ml. of sulfuric acid and evaporate to fumes. Heat until any free sulfur that precipitates disappears. Allow to cool. Dilute with 30–40 ml. of water, heat to boiling and keep hot until ferric sulfate has dissolved (copper will all be in solution). Filter into a small beaker and wash the residue at least six times with hot water, using small portions at a time. The volume of the filtrate need not exceed 75–100 ml. This contains all of the copper.

Isolation of Copper.—Two optional procedures for separating copper from interfering elements are given. Procedure *A*, by which copper is precipitated by an element more positive in the electromotive series; procedure *B*, by which copper is separated as sulfide.

Procedure A. Precipitation of Metallic Copper.—Place in the beaker containing the copper solution a piece of heavy sheet aluminum (1.5 inches square) or a strip of aluminum bent in form of a triangle, or add 1–2 grams of pure granulated aluminum. If a sheet is used, bend the corners at right angles so it will not lie flat in the beaker. (The sheet may be used repeatedly as it is not attacked to any great extent by the nitric acid subsequently used.) Heat the solution to boiling (beaker covered) and keep at this temperature for about 10 minutes. All of the copper will precipitate, an equivalent amount of aluminum dissolving. If the action is sluggish, add 2 or 3 drops of hydrochloric acid. Wash down the cover and sides of the beaker with hydrogen

sulfide water. (This precipitates any trace of copper in the solution and prevents oxidation of the copper.)

Decant the solution through a filter and rinse the metallic copper into the filter with a jet of the hydrogen sulfide water, leaving the aluminum as clean as possible in the beaker. Save this. Wash the precipitate 6 times with hydrogen sulfide wash water, allowing to drain, but following up immediately with more solution, until the washing is complete. (Copper will oxidize if allowed to stand exposed to the air. Hence the washing should be completed as soon as possible.)

Solution of the Copper.—Punch a hole in the filter and wash the copper into a beaker with a jet of water, using as little as possible. (If much copper is present, open the filter on a watch glass and wash the precipitate into a beaker. Again fold the filter and place in the funnel over the beaker.) Pour 5 ml. of conc. nitric acid over the aluminum, which still contains a little of the copper. When all of this has dissolved, pour the nitric acid solution over the filter, catching the acid in the beaker containing the bulk of the copper. (Removing the beaker, place the one containing the foil under the filter.) Cover the beaker containing the copper and boil until the metal is in solution and again place under the filter funnel. Wad the filter paper loosely in the funnel. Pour over this filter 5–10 ml. of bromine water, catching the solution in the beaker containing the copper; this should impart a yellow color to the copper solution. Wash the filter 6 times with water, pouring the water first into the beaker with the aluminum and from this over the wadded filter.

Concentration.—Boil the combined solution down to about 25 ml. The bromine will be expelled. Add a small excess of ammonia; the free acid is neutralized and the solution smells of ammonia. Again boil to expel the excess of ammonia. The solution should still smell faintly of NH_3. Add glacial acetic acid until slightly acid (litmus test); 5 ml. should be sufficient. Cool thoroughly.

In place of isolating copper as the metal it may be precipitated as sulfide according to the procedure given in Procedure *B*.

Cadmium, antimony and tin will accompany copper if present in the solution.

Procedure B. Thiosulfate Precipitation of Copper Sulfide.—Dilute the solution to about 250–300 ml. and add 10 ml. of 50% solution of sodium thiosulfate (1 : 2) and heat gently, the solution darkening and copper sulfide precipitating as the solution begins to boil. Twenty minutes is ample for complete precipitation of the sulfide. Filter off the CuS and wash with water to remove iron, etc. Fold the filter over the precipitate, transfer to a 25-ml. porcelain crucible and heat till the paper chars and then ignite gently until the paper is consumed. Dissolve the residue in 5 ml. of conc. nitric acid, heating gently, until the brown fumes are expelled. Transfer to a small beaker by means of a jet of water (10–20 ml.) and again heat to expel oxides of nitrogen. Cool and add ammonia drop-wise until the precipitate that first forms re-dissolves. Heat to expel the excess of ammonia, the solution having but a faint odor of the reagent. Cool and add drop-wise glacial acetic acid until the precipitate that first forms re-dissolves and the solution is clear. Add 3–5 drops in excess. Heat gently 4–5 minutes and cool thoroughly.

Titration.—Procedure following *A* or *B* above.

Add solid crystals of potassium iodide in just sufficient amount to redissolve the cuprous iodide that first forms and titrate immediately with standard

thiosulfate until the reddish-brown color fades to a yellow. Add starch indicator and cautiously complete the titration drop-wise until a drop produces a colorless solution, stirring the solution during the titration.

Multiply the ml. of thiosulfate required by its factor in terms of copper to obtain the weight of copper in the sample.

NOTES.—The amount of copper in the sample should be preferably within the limits of 50 to 150 mg. (which permits a titration of convenient volume without undue dilution).

Since a yellow color may be due to other causes than to free iodine, it is advisable to make a preliminary titration by adding the starch indicator before starting titration with thiosulfate. In a check run the starch is added upon neutralizing the greater part of the free iodine. This precaution prevents overrunning the end-point, which one is apt to do when depending upon a color change of iodine brown to yellowish-brown due to a trace of free iodine.

In Procedure *B*, "Boiling the nitric acid solution of the copper oxide with water and the final boiling with acetic acid effects the expulsion of any oxidizing agents. It is thought that salts depress the ionization of the excess acid which is so great with acetic acid when the volume is small that the liberation of iodine is not free and rapid. Hence a premature end-point may occur. By evaporating the nitric acid solution to low bulk and by boiling off the excess ammonia, the salts that may interfere are reduced to a minimum. The volume of the solution before titration should be less than 50 ml. If the ore be high in arsenic or antimony the copper may be separated as the thiocyanate and then ignited."[15]

SHORT IODIDE METHOD FOR COPPER

The method takes advantage of the repression of ionization of iron by addition of potassium fluoride to a neutral or acetic acid solution containing the ferric salt. Ag, As, Bi, Cd, Co, Fe, Hg, Mn, Mo, Ni, Pb, Sn, U, Zn do not interfere. Cr forms an insoluble sulfate, which holds Cu; hence avoid using H_2SO_4. V interferes.

PROCEDURE

Decomposition.—0.5 to 1.0 gram of the material is decomposed by 10–15 ml. hydrochloric acid and 5 ml. nitric acid and warming. When the action has ceased, 5 ml. of sulfuric acid are added and the solution taken to strong fumes. (In presence of chromium the sulfuric acid is omitted, the solution being taken to near dryness, 10 ml. more HCl are added and the evaporation repeated to expel HNO_3.) Thirty ml. water are now added to the cooled solution and the solution boiled to dissolve any salt that has crystallized out. Five ml. bromine water are added to oxidize any arsenic or antimony that may be present and the excess expelled by boiling.

Ammonium hydroxide is now added until the solution shows an alkaline reaction, the odor of ammonia being evident in the solution. The mixture is now acidified with glacial acetic acid (5–10 ml. should make the solution decidedly acid). Two grams (approximately 2 ml.) of solid potassium fluoride are now added to precipitate iron; additional fluoride may be necessary if the supernatant solution is colored by iron. The solution is boiled for a minute or so and then cooled under the tap.

To the cold solution 5 ml. of a 50% solution (or its equivalent of 2 g. of KI) of potassium iodide are added, together with 5 ml. of starch solution.

[15] E. H. Smith, Chemist-Analyst, 18, 6 (1929).

The liberated iodine is now titrated with 0.1 N thiosulfate, to the point where one drop destroys the blue color. It is advisable to add 1–2 ml. more of potassium iodide, and if a blue color results, to add more of the thiosulfate until the color is destroyed.

$$1 \text{ ml. } 0.1 \text{ N } Na_2S_2O_3 = 0.00636 \text{ g. Cu.}$$

NOTE.—The additional iodide is occasionally necessary owing to its consumption by Co, Ni, U, Mo, Pb, Bi, Zn, As^5, Sb^5, etc.; however As^3, and Sb^3 interfere.

PARK MODIFICATION OF THE SHORT IODIDE METHOD[16]

Procedure.—Treat a suitable sample of the ore, slag, etc. with nitric acid until all copper is in solution. Boil down to about 5 ml., add 30 ml. of water, and boil to assure complete solution of soluble matter and also to expel oxides of nitrogen. Filter and wash the residue well with hot dilute nitric acid. If the residue is small in amount or light colored, filtration may be omitted. Concentrate the solution by boiling to about 30 ml., cool, add ammonium hydroxide until the iron is all precipitated and the solution smells faintly of ammonia. Avoid adding an excess. Add 2 g. of ammonium bifluoride, shake, add 1 g. of potassium biphthalate,[17] shake, add 3 g. of potassium iodide and shake the vessel. Titrate at once with thiosulfate, approaching the endpoint slowly. When near the end-point add sufficient starch solution. After the blue color has been discharged it should not return within 30 minutes.

Note on the Endpoint of the Iodide Method for Copper.[18]—The addition of a little soluble thiocyanate just before the endpoint is reached in the final titration with $Na_2S_2O_3$ gives a slight further liberation of iodine and a sharper endpoint is obtained. If the thiocyanate is not added the reduction of cupric ion by iodide is not quite complete.

METHODS OF COPPER ANALYSIS, C. & A. COPPER CO., AJO, ARIZONA

Copper by Iodate Method.—Weigh 1.25 to 5 grams of ore into a 250-ml. Erlenmeyer flask. Add 15 ml. Acid Mixture (p. 373), 3 or 4 drops of HF and evaporate to dryness (or until residue is white). Cool, add 75 ml. of water to dissolve salts. Make just neutral with NH_4OH (first permanent formation of ferric hydroxide). Add exactly 5 ml. HCl and 10 ml. Na_2SO_3 solution. If a brown precipitate of ferric hydroxide appears add a few drops of HCl to neutralize the excess of ammonia and to have a slight excess of HCl. (High iron ores require more Na_2SO_3 until all iron is reduced and 2 or 3 more ml. of HCl.) Add 10 ml. KCNS solution and heat until solution begins to boil. A red coloration indicates unreduced iron or an excess of HCl. In this case add more Na_2SO_3 solution. The precipitate in the flask should be white. Filter through double filter papers, B & A grade A, on top of grade B (Whatmann No. 1),

[16] B. Park, Ind. Eng. Chem. Anal. Ed. 3, 77 (1931).

[17] According to Crowell et al., Ind. Eng. Chem. Anal. Ed. 8, 9 (1936), the addition of the potassium biphthalate is not necessary.

[18] Foote and Vance, J. Am. Chem. Soc., 57, 845 (1935); Ind. Eng. Chem., Anal. Ed. 8, 119 (1936).

both 12½ cm. A yellow coloration on the paper shows a deficiency of HCl. Add a few drops to the flask. Wash the flask twice and filter three times to insure the removal of excess KCNS. During the removal of the paper from the funnel, give the funnel a circular motion to get any copper-sulfo-cyanate that may have collected above the paper. Remove and wash stopper. Add 60 ml. of soluble starch solution and titrate rapidly with standard solution of potassium iodate, shaking flask with rotary motion. When deep blue color of the starch begins to turn brown, stop titration, stopper flask and shake, continue titrating until the disappearance of the brown to light green. The end-point is very sharp. If the ore is low in copper or gives a dirty precipitate, 3 ml. of carbon tetrachloride should be used as an indicator. Titrate to the disappearance of the pink color of the tetrachloride.

Standard Potassium Iodate Solution.—Dissolve 265.14 grams C.P. Potassium Iodate in 18 liters of water. Standardize, using standard copper ore as under Iodate Method. One ml. = .0025 gram Cu.

Standard Potassium Thiocyanate Solution.—This solution is used for the back titration in the Iodate Method. Dissolve 4.414 grams C.P. KCNS in 1 liter of water. One ml. KCNS = .1 ml. .0025 KIO_3.

Acid Mixture.—To 250 ml. of HNO_3 saturated with $KClO_3$ add 500 ml. HNO_3, then 250 ml. of concentrated H_2SO_4. Cover with wet cloth, insert stopper, give a shake or two, then remove the stopper at once and let the gas escape. Continue until well mixed.

Sodium Sulfite Solution.—Dissolve 200 grams of technical sodium sulfite in 1 liter of water.

Potassium Thiocyanate Solution.—Dissolve 50 grams of KCNS C.P. in 1 liter of water.

Oxide Copper by Iodate Methods.—Weigh 2.5 g. to 10 g. of ore into a 250-ml. casserole, add 20 ml. water and remove metallic iron with an electromagnet. Wash ore into 250-ml. beaker and dilute to 50 ml. with hot water. Add 10 ml. of Na_2SO_3 solution and 10 ml. (1 : 1) H_2SO_4. Boil two minutes. Filter through 15 cm. B & A grade paper into 250-ml. Erlenmeyer flask and wash the insoluble three times with hot water. Complete as under the above Iodate Method.

POTASSIUM CYANIDE METHOD

This procedure is largely employed on account of its simplicity, although it does not possess the degree of accuracy of the Iodide Method. The procedure depends upon the decoloration of an ammoniacal copper solution by potassium cyanide.

The operations of the standardization of potassium cyanide and of making the assay should be as near alike as possible. If iron is present in the assay it should be added to the standard copper solution titrated, in order to become accustomed to the end-point in its presence.

Silver, nickel, cobalt, cadmium, and zinc interfere and should be removed if present in appreciable quantities. Precipitation of metallic copper by aluminum powder, as directed under Separations, is recommended as a procedure for iron ores and briquettes. In presence of smaller amounts of iron, the titration may be made in presence of iron suspended in the solution. It is not

advisable to filter off this precipitate, as it invariably occludes copper. With practice, the shade of color the iron precipitate assumes at the end of the reaction serves as an indicator, so that the operator is assisted rather than hindered by its presence.[19]

$$2Cu(NH_3)_4SO_4 \cdot H_2O + 7KCN = K_3NH_4Cu_2(CN)_8 + NH_4CNO + 2K_2SO_4 + 6NH_3 + H_2O.$$

Standard Potassium Cyanide Solution.—Thirty-five grams of the salt are dissolved in water, then diluted to 1000 ml.

Standardization.—0.5 gram of pure copper is dissolved in a flask by warming with 10 ml. of dilute nitric acid (sp.gr. 1.2), the nitrous fumes expelled by boiling, the solution neutralized, diluted and titrated as directed under Procedure. If iron is present in the samples titrated, it is advisable to add iron to the standard copper solution as directed above.

$$\frac{0.5}{\text{ml. KCN solution}} = \text{wt. Cu per ml. of standard KCN.}$$

Procedure.—The solution containing the copper is neutralized with sodium carbonate or hydroxide, the reagent being added until a slight precipitate forms. One ml. of ammonium hydroxide is now added and the solution titrated with standard potassium cyanide solution. The blue color changes to a pale pink; finally a colorless solution is obtained. In presence of iron, when the copper is in excess of the cyanide, the iron precipitate possesses a purplish-brown color, but, as this excess lessens, the color becomes lighter until it is finally an orange brown, the solution appearing nearly colorless. The reagent should be added from a burette drop by drop as the end-point is approached.

$$\text{Ml. KCN} \times \text{factor per ml.} = \text{weight Cu in assay.}$$

VOLUMETRIC METHODS BASED UPON THE PRECIPITATION OF COPPER AS CUPROUS THIOCYANATE

IODATE METHOD[20]

A thiocyanate salt is oxidized by a series of reactions which when completed has this form: $4CuCNS + 7KIO_3 + 14HCl = 4CuSO_4 + 7KCl + 7ICl + 4HCN + 5H_2O$. Cyanates other than copper, lead and antimony must be absent from the precipitate of cuprous thiocyanate. This precipitate together with

[19] Sutton, "Volumetric Analysis." Davies, Chem. News, 58, 131 (1888). J. J. and C. Beringer, Chem. News, 49, 3 (1884). Steinbeck, Z. anal. Chem., 8, 1 (1869).

[20] Jamieson, Levy and Wells, J. Am. Chem. Soc., 30, 760 (1908). Price and Meade, "Technical Analysis of Brass," Sec. Ed., p. 84.

the filter paper is placed in a 250-ml. glass-stoppered bottle and 5 ml. chloroform, 20 ml. water and 30 ml. concentrated hydrochloric acid added.

A certain amount of standard potassium iodate solution (11.784 grams KIO_3 per liter, 1 ml. = 2 milligrams copper) is added from a burette. When the bottle is thoroughly shaken, a violet color appears in the stratum of chloroform which may increase in depth of tint and then fade with each addition of iodate solution. Disappearance of color determines the end-point. The KIO_3 solution is very stable. The same layer of chloroform can be used for successive determinations by decanting only the liquor carrying the paper pulp. The immediate coloring of the chloroform on addition of a precipitate to the bottle is due to the reaction with residual ICl and has no harmful effect on the determination.

PERMANGANATE METHOD[21]

Although this method is based upon these reactions: $CuCNS+NaOH = CuOH+NaCNS$ and $5HCNS+6KMnO_4+4H_2SO_4 = 3K_2SO_4+6MnSO_4 +5HCN+4H_2O$, solution of the copper salt by the method of manipulation and possibly incompletion of oxidation makes necessary the use of an empirical factor. Theoretically the iron value multiplied by 0.1897 gives the copper value of permanganate. By this method the Fe to Cu factor may be from 0.192 to 0.2. The thiocyanate precipitate is decomposed on the filter with boiling 8% NaOH. The filter is washed with hot water. After making the filtrate acid with dilute H_2SO_4, titration of the solution to permanent tint is made with standard $KMnO_4$ solution having a strength of 1 ml. equivalent to about 1 mg. copper.

DEMOREST'S METHOD[22]

Precipitation of cuprous thiocyanate is from a nearly boiling 75–100 ml. solution containing ammonium sulfate, about 3 grams ammonium tartrate and 1 ml. free sulfuric acid. Five per cent solution of sodium sulfite is first added, then slowly, with stirring, 5% solution of potassium thiocyanate. The coagulated precipitate is collected from the hot liquid in an asbestos-lined Gooch crucible and washed thoroughly. The precipitate is decomposed in the crucible by pouring on it hot 10% NaOH. The residue of CuOH in the crucible is washed well with hot water.

The alkaline filtrate is warmed to 50° C. and a few ml. of standard permanganate solution introduced. At 10 or 5 ml. intervals during the titration, a drop of the green solution is placed on a paraffined white plate together with a drop of conc. hydrochloric acid. When the red color of this test drop becomes faint on addition of a drop of a 10% solution of $FeCl_3$, 30 ml. of 50% H_2SO_4 are added and the flask shaken until all the MnO_2 is dissolved. The characteristic end-point will appear on addition of very little more permanganate. This method has the merit of not requiring an empirical factor, the copper value of the permanganate being 0.1897 times that of the iron.

[21] Low, "Technical Methods of Analysis." Chapter on Copper has table of empirical factors, compiled by G. A. Guess.

[22] J. Ind. Eng. Chem., 5, 215 (1913).

VOLHARD'S METHOD

The copper is precipitated with a standard solution of alkali thiocyanate. After filtering and washing the precipitate free of reagent, the excess is titrated with standard silver nitrate solution.

GARRIGUE'S METHOD

The precipitate of cuprous thiocyanate is collected in a Gooch crucible, decomposed in a casserole with an excess of hot, standard NaOH. The cuprous hydrate formed is filtered, washed and the excess alkali titrated with standard HCl. The reactions are: $CuCNS+NaOH=CuOH+NaCNS$ and $NaOH+HCl=NaCl+H_2O$.

COLORIMETRIC DETERMINATION OF SMALL AMOUNTS OF COPPER

DIETHYL DITHIO CARBAMATE METHOD[23]

A 0.1% solution of $(C_2H_5)_2NCSSNa$ (prepared by interaction of CS_2 and diethylamine in the presence of alkali) in water is used as the reagent. With 0.1 part of copper per million of solution the reagent gives a distinct golden brown color, and with 1 p.p.m. of Cu the solution becomes cloudy and a very deep golden brown color develops. Co, and ferrous and ferric iron give brown precipitates; lead and zinc give white precipitates. An extraction method is therefore used:

Procedure.—Dissolve 2 g. of citric acid in the solution, add ammonia until the pH is 9 or larger and dilute to 70 ml. Add 10 ml. of the reagent and extract immediately with four successive portions (2.5 ml. each) of CCl_4. If the final extract contains more than a trace of color continue the extractions. Compare the color in a colorimeter with that of standard solutions prepared in similar manner. The method may be applied to solutions containing Al or Zn up to 0.5 g., Cr^{III} up to 2 g. and to Mn up to 2 g. if no more than a trace of Fe is present. The color is stable for at least an hour, and the reagent is stable for several weeks if preserved in an amber colored bottle.

POTASSIUM ETHYL XANTHATE METHOD

The method is based upon the fact that potassium ethyl xanthate produces a yellow-colored compound with copper: The reagent added to a solution

[23] Callan and Henderson, Analyst, 54, 650 (1929). Haddock and Evers, Analyst, 57, 495 (1932).

containing traces of copper will produce a yellow color varying in intensity in direct proportion to the amount of copper present. Larger amounts of copper with the reagent produce a bright yellow precipitate of copper xanthate. Small quantities of iron, lead, nickel, cobalt, zinc, or manganese do not interfere. The procedure is especially valuable for determination of the purity of salts crystallized in copper pans.

Special Solutions. ***Stock Solution of Copper Sulfate.***—3.928 grams $CuSO_4 \cdot 5H_2O$ are dissolved in water and made up to a volume of 1000 ml. One ml. is equivalent to 0.001 gram Cu.

Standard Copper Sulfate.—Ten ml. of the stock solution are diluted to 1000 ml. with distilled water. One ml. = 0.00001 gram Cu.

Potassium Ethyl Xanthate Solution.—One gram of the salt is dissolved in 1000 ml. of water. The solution is kept in an amber-colored glass-stoppered bottle.

Procedure.—Five grams of the substance are dissolved in 90 ml. of water (see note) and the solution poured into 100-ml. Nessler tube; 10 ml. of the potassium xanthate reagent are added and the solution mixed by means of a glass plunger. To a similar tube containing 50 or 60 ml. of water are added 10 ml. of the xanthate reagent and then gradually drop by drop the standard copper solution from a 10-ml. burette (graduated in $\frac{1}{10}$ ml.) until the colors in both tubes match.

If a = grams of the substance taken for analysis, b = number of ml. standard copper solution required to match the sample; then $b \times 0.00001 \times 100 \div a = \%$Cu.

NOTES.—The amount of the substance to be taken varies according to its copper content. The greater the copper contamination of the salt, the less sample required. The solution should be neutral or only very slightly acid.

In place of the Nessler tubes the special colorimetric apparatus described under Titanium and under Lead may be used. A very weak copper standard will be required for the comparison tube.

If the substance is insoluble in water the copper is rendered soluble by treatment with nitric acid. Hydrochloric acid is added and the nitric expelled by evaporation. The substance is taken up with water and the insoluble residue filtered off.

Starch and organic matter are destroyed by addition of 10 ml. 10% sodium hydroxide +10 ml. of saturated sodium nitrate solution, then evaporating to dryness and igniting. Hydrochloric acid is now added to expel the nitric acid as directed above.

In dealing with a flotation concentrate containing oil, the sample should be taken to fumes with nitric acid, otherwise the color is apt to be green instead of blue.—C. Y. Pfoutz.

FERROCYANIDE METHOD FOR DETERMINATION OF SMALL AMOUNTS OF COPPER

By this colorimetric method it is possible to detect one part of copper in 2,500,000 parts of water. The procedure depends upon the purplish to chocolate-brown color produced by potassium ferrocyanide and copper in dilute solutions. The procedure is applicable to the determination of copper in water and may be used in presence of a number of elements that occur in slags. Iron also produces a colored compound with ferrocyanide (1 part Fe detected in 13 million parts H_2O), so this element must be removed from the solution before testing for copper.

Solutions. ***Standard Copper Solution.***—0.393 gram $CuSO_4 \cdot 5H_2O$ per liter. One ml. = 0.0001 gram Cu.

Ammonium Nitrate.—100 grams of the salt per liter.

Potassium Ferrocyanide.—Four grams of the salt per 100 ml. of solution.

Procedure.—A volume of 5 to 20 drops of potassium ferrocyanide, according to the amount of copper present in the solution, is placed in a tall, clear, glass cylinder or Nessler tube of 150 ml. capacity, 5 ml. of ammonium nitrate solution added and then the whole or an aliquot portion of the neutral solution of the assay. The mixture is diluted to 150 ml. The same amount of ferrocyanide and ammonium nitrate solutions are poured into the comparison cylinder, placed side by side with the one containing the sample, on a white tile or sheet of white paper. The standard copper solution is now run from a burette into the comparison cylinder, stirring during the addition, until the color matches that of the assay. The number of ml. required multiplied by 0.0001 gives the weight of copper in the sample contained in the adjacent cylinder.

$$\frac{\text{Amount of Cu} \times 100}{\text{Wt. of sample compared}} = \%\ \text{Cu in the sample.}$$

NOTES.—The solution must be neutral, as the copper compound is soluble in ammonium hydroxide and is decomposed by the fixed alkalies. If the solution contains free alkalies, it is made slightly acid and then the acid neutralized with ammonia, added in slight excess. This is boiled to expel the excess of ammonia, and then tested according to the directions under "Procedure." Solutions containing free acids are neutralized with ammonia.

Iron may be removed by precipitation with ammonia. As this hydroxide occludes copper, the precipitate should be dissolved and reprecipitated to recover the occluded copper.

Determination of copper in water is accomplished by evaporating a quantity of water to dryness, taking up the residue with a little water containing 1 ml. nitric acid, the residue having been ignited to destroy organic matter, precipitating iron with ammonia, as directed above, and determining copper in the filtrate.

The colorimeter used in determination of traces of lead and for the colorimetric determination of titanium may be employed in place of the Nessler tubes.

AMMONIA METHOD FOR DETERMINING SMALL AMOUNTS OF COPPER

In the absence of organic matter, nickel, and elements giving a precipitate with ammonia, copper to an upper limit of 10 milligrams can be determined by comparison of the depth of the blue tint of its ammonium solution with a temporary or permanent standard copper solution of equal volume. Because copper in ammoniacal solution combines with the cellulose of filter paper, clarification of such a solution should be through asbestos. Permanent standard solution of copper sulfate, free of nitrate, if kept cool and away from the direct sunlight, lasts for a long time.[24]

[24] Heath, J. Am. Chem. Soc., 19, 21 (1897).

COLOR METHOD FOR COPPER[25]

The following methods, taken from the work of Keffer and McNeil, are standard procedures used by the Anaconda Copper Mining Company.

a. Mill Tailing.—Weigh 5 g. into a 150-ml. beaker, add 1 to 2 g. of potassium chlorate, and 25 ml. of concentrated nitric acid. Place on the steam plate for at least 1 hour, or until the volume of the acid has been reduced to about 10 ml. Wash down the side of the beaker with 15 ml. of water, remove from the steam plate, and dilute to 100 ml. with cold water. When cold, precipitate the iron and aluminium hydroxides by the addition of an excess of ammonia (1 : 1). Filter through an 18.5-cm. C. S. & S. paper, No. 595 or 597, receiving the filtrate in a square bottle of 450-ml. capacity. This bottle must be of clear, colorless glass. Rinse the beaker once, pour onto the filter, and wash the precipitate once more with hot water, allowing the precipitate to drain thoroughly each time. Dilute to 250 ml. volume and compare with the tailings standards. Read to the nearest 0.05, and divide the result by 5.

b. Slime Tailing.—Weigh 2 g. into a 300-ml. casserole, add 1 to 2 g. of potassium chlorate and 10 ml. of bromine water, and gently shake until the pulp is thoroughly moistened. Evaporate to dryness, cover with a watch glass, and bake on the hot plate for 30 minutes. Place on an asbestos-covered board, allow to cool, remove the cover glass, and wash down the sides of the casserole with 5 to 8 ml. of water. Then add 15 ml. of sulfuric acid (1 : 1), place on the hot plate, and evaporate until heavy fumes of sulfur trioxide are evolved. Cool, add 20 ml. of nitric acid (1 : 1), and boil for 5 minutes. Again cool, and dilute with water to about 75 ml. volume. Precipitate with ammonia (1 : 1) and proceed as for mill tailing, dividing the final result by 2 instead of 5.

c. Reverberatory Slag.—Treat 2 g. in a 250-ml. beaker with 10 ml. of hot hydrochloric acid, pouring in the acid in such a manner as to prevent the slag from caking on the bottom of the beaker. Break up any lumps that may form. Digest on the steam plate for 20 minutes, and then add 5 ml. of nitric acid. Stir each assay with a glass rod to break up any gelatinous or undecomposed material, and allow to digest 20 minutes longer, after which time the slag should be thoroughly decomposed. Should the slag contain so much lime as to be difficult to decompose by the foregoing treatment, add 3 ml. of hydrofluoric acid and evaporate to a pasty mass. Again stir thoroughly to break up any large gelatinized particles and wash down the side of the beaker with a small amount of water. Remove from the hot plate, allow to cool, and dilute to 100 ml. with cold water. Add an excess of ammonia (1 : 1) while thoroughly stirring. Filter on an 18.5-cm. paper, and wash out the beaker with warm water. Allow to drain thoroughly, and wash twice with warm water. Dilute to 250 ml. with cold water and compare with the reverberatory slag standards, reading directly to the nearest 0.05% copper.

d. Blast-furnace Slag.—Weigh 3 g. into a 150-ml. beaker. Mix thoroughly with 10 ml. of water. Add 5 ml. of nitric acid and digest 10 minutes until gelatinized. Add 5 ml. of hydrochloric acid, mix thoroughly with a glass rod to break up gelatinized particles, and digest for 20 minutes. Dilute and neutralize

[25] Methods in Non-Ferrous Metallurgical Analysis, by Robert Keffer, Late Chief Chemist, and Charles L. McNeil, Assistant Research Chemist, Anaconda Copper Mining Company. McGraw-Hill Book Co., Publishers.

with ammonia (1 : 1) the same as for reverberatory slag. Filter, and compare with the blast-furnace slag standards, reading to the nearest 0.05% copper.

e. Standard Colors.—Prepare a standard copper solution by weighing 1 g. of pure copper foil, free of oxides, etc. Dissolve in 7 ml. of concentrated nitric acid, and allow to stand until all nitrous fumes have disappeared. Dilute to 500 ml. with cold distilled water, add 3 ml. of concentrated sulfuric acid, and dilute to 1 liter with cold distilled water. Mix thoroughly before using. The standard colors are made up from the standard copper solution, according to the following table. Add 200 ml. of cold distilled water to the clean color bottle, followed by the proper amount of ammonia as indicated in the table. Then

COLOR COPPER STANDARDS

Copper, %	Reverberatory slag		Blast-furnace slag		Tailing	
	Milliliters of NH_4OH	Milliliters of standard copper solution	Milliliters of NH_4OH	Milliliters of standard copper solution	Milliliters of NH_4OH	Milliliters of standard copper solution
0.20	5	3.2	5	4.4	5	1.5
0.25	..	....	6	5.5		
0.30	6	4.6	7	6.7	5	2.7
0.35	..	....	8	7.9		
0.40	7	6.1	9	9.1	6	3.8
0.50	8	7.9	..	...	7	4.7
0.60	9	9.7	..	...	8	5.7
0.70	10	11.4	..	...	9	6.6
0.80	10	13.2	..	...	10	7.6
0.90	..	....	..	...	10	8.5
1.00	..	....	..	...	10	9.5
1.20	..	....	..	...	10	10.4
1.40	..	....	..	...	10	13.2
1.60	..	....	..	...	10	15.2

the number of milliliters of the standard copper solution as stated in the table are added from a burette, and the solution diluted to 250 ml. The standards must be made up once a week to insure good results, as they gradually fade on standing. The colors should be read against a white background. A rack with places for each standard bottle, and sufficient space to set the assay beside each standard bottle in turn, should be provided. A strip of white oilcloth forms a good background, and may be readily cleaned. A strong, diffused light is necessary for accurate work.

f. A green tint instead of a clear blue is sometimes obtained. This can be avoided by closely measuring the amounts of reagents added, and especially taking care to have the solutions cold before adding the ammonia.

HYDROGEN SULFIDE METHOD

In the absence of elements precipitated by hydrogen sulfide, copper to the limit of about 1 milligram, in a solution not too strongly acid with sulfuric or hydrochloric acid, may be determined by comparison of its sulfide with that of

a known quantity of copper in equal volume and similarly treated. The liquid should be cold and the passage of the hydrogen sulfide stopped before the compound coagulates.

NOTE.—Either the ammonia or the hydrogen sulfide method is applicable to the determination of the copper not deposited in the operation of the electrolytic method.

DETERMINATION OF IMPURITIES IN BLISTER AND REFINED COPPER

Introduction.—In the complete analysis of copper the following impurities are generally determined: silver, gold, lead, bismuth, arsenic, antimony, selenium, tellurium, iron, zinc, cobalt, nickel, oxygen, sulfur, and, less commonly, tin and phosphorus. In high grades of blister and in refined copper the percentage of these impurities is very low, the blister copper usually averaging over 99.0% copper with silver and the refined copper over 99.93% of the metal. The principal impurity in the refined element is oxygen, which may be present to the extent of .02 to .15%, the remaining impurities being in the third decimal place. From this it is readily seen that large samples are required for the accurate determination of these constituents. The amount of sample taken in blister copper depends upon the grade of copper analyzed. The impurities in this vary from tenths of a per cent to thousandths, as the metal from one locality may contain quite appreciable amounts of a constituent, which may be present only in extremely small quantities or not at all in copper from a different section. In usual practice it is customary to take from 10 to 50 grams of blister and 50 to 500 grams of refined copper for analysis, depending upon the purity of the material. If a larger sample than 50 grams is taken, it is necessary to divide the material into several lots, and, after removal of the bulk of copper and isolation of the impurities, to combine the filtrates or residues containing the constituents sought.

In the procedures the smallest amount of sample, 10 grams, is taken as the basis of calculation for amounts of reagents used. For larger samples, in the initial treatment for removal of copper, proportionately larger amounts of the reagents are required, i.e., multiples of from 2 to 5 times the amount stated. A 50-gram sample is the largest amount of material handled in one lot.

Scrupulous care must be exercised throughout the analysis to prevent contamination of the sample or reagents, and to avoid loss of constituents. The reagents used should be free from the substance sought or from interfering substances. It is the practice to carry blank tests of the reagents through under

conditions similar to a regular analysis for iron, lead, zinc, arsenic, antimony and sulfur.

It is found best to determine the impurities in several portions, i.e., gold and silver by assay; bismuth and iron in one portion; lead, zinc, cobalt, and nickel in a second; arsenic, antimony, selenium, and tellurium in a third; and separate portions for sulfur, oxygen, phosphorus and tin, when these are occasionally required.

DETERMINATION OF BISMUTH AND IRON

The same general procedure applies to blister copper and refined copper for bismuth determination, but, refined copper, due to the very minute amount of iron present, calls for a very much more delicate method for iron determination. This procedure is described on page 383.

The minute amount of iron taken up from the drill and mill in sampling blister copper is of no practical consequence. The sample should be examined carefully for small fragments of steel which sometimes break away from the drill. These pieces are easily distinguished and should be removed from the sample.

Separation of Copper. *Amount of Sample.*—Blister copper 10 to 25 grams, refined copper 100 to 500 grams. The drillings are dissolved in a large beaker in 40 ml. of nitric acid per 10-gram sample and the free acid expelled by boiling. The solution should not become basic during the evaporation. Water is added to make the volume 130 ml. per 10 grams or proportionately more for larger samples. Ammonia is now added in sufficient excess to hold the copper in solution and 5 ml. of saturated ammonium carbonate solution and the sample diluted to 200 ml. (25 ml. $(NH_4)_2CO_3$ per 50 grams, and dilution to 1000 ml.). The beaker is placed on the steam bath for several hours, preferably over night. The solution is filtered hot (to avoid crystallization of the copper salt), the first 100 ml. being refiltered, and the residue washed with hot water containing a little ammonia. By this procedure the copper passes into the filtrate and bismuth and iron remain in the residue on the filter.

Separation of Iron and Bismuth.—The precipitate is dissolved in warm, dilute hydrochloric acid (1 : 3), ammonia added to the solution in sufficient amount to almost neutralize the acid and the solution then saturated with hydrogen sulfide. After settling some time, the precipitate containing bismuth sulfide is filtered off, iron passing into the solution.

Determination of Iron.—Hydrogen sulfide is expelled by boiling the filtrate, and iron oxidized by addition of hydrogen peroxide, or potassium chlorate (nitric acid should not be used). The solution is evaporated to dryness and iron then determined in the residue by the stannous chloride method, details of which may be found in the chapter on Iron.

Determination of Bismuth.—The sulfides remaining on the filter are dissolved in nitric acid, the solution evaporated with sulfuric acid to SO_3 fumes to expel nitric acid, the concentrate diluted with water, and lead filtered off. Bismuth is precipitated in the filtrate by addition of ammonia in slight excess, followed by 10 ml. of a saturated solution of ammonium carbonate, and boiling. The precipitate is settled for several hours or over night if preferred, and then separated by filtration. This is now dissolved in the least amount of nitric

acid, added to the filter drop by drop from a burette and bismuth determined in the solution by the cinchonine iodide method, given in detail in the chapter on Bismuth.

NOTES.—An excess of nitric acid or the presence of cadmium, lead, silver, or hydrochloric acid interferes with the colorimetric procedure.

In analysis of refined copper several 50-gram portions are taken for analysis, ten such portions on a 500-gram sample; the filtrates, obtained upon dissolving the residue freed from copper, are combined and bismuth determined on this combined solution.

IRON IN REFINED COPPER (ELECTROLYTICALLY REFINED AND CAST INTO SHAPES)

This grade of copper rarely contains more than .0005% of iron. A drilled sample exposes comparatively large surfaces to contamination from the drill. Washing of the drillings with Hydrochloric Acid does not insure entire removal of this surface iron.

The following method was developed at the Raritan Copper Works:[25]

DETERMINATION OF IRON IN WIRE BAR COPPER

A slice of copper about 1 inch thick is cut from *somewhere* near the middle of the bar. This slice is again cut so as to obtain a one inch cube (approximately).

Digest the cube of copper in dilute HCl (1 to 3) at about 50° C. for two hours. Wash thoroughly in distilled water, wipe the surface and weigh.

Dissolve in 2000 ml. beaker with nitric acid and take an aliquot so as to obtain a portion representing 100 gm. of sample.

Wash all Apparatus Including Watch Glasses and Funnels with HCl and Run a Blank Using Equal Quantities of all Reagents.

Dilute with 500 ml. of distilled water and add ammonia until all basic salts have been dissolved. Bring to boiling and allow to stand one hour. Filter on 15 cm. 1F Munktell paper. *Keep beaker and funnel covered as much as possible.*

Wash once with hot water and dissolve with HCl (1 to 3) into 300 ml. beaker. Dilute to 200 ml., make slightly ammoniacal. Boil and let stand 15 minutes. Filter on 12½ cm. 1F Munktell paper. Wash once with hot water.

Dissolve the precipitate off of the paper with 5 ml. hydrochloric acid (sp.gr. 1.19) and wash with water, keeping the volume below 40 ml. Transfer to Nessler tube and add 10 ml. NH_4CNS solution.

To the comparing Nessler tube, add 5 ml. hydrochloric acid (1.19), water and finally 10 ml. NH_4CNS solution. Make up to 50 ml. mark and add, drop by drop, standard $Fe_2(SO_4)_3$ solution. (1 ml. equals .0005 gms. of iron.) 1 ml. standard solution equals .0005% iron in sample.

Solutions.—NH_4CNS—23 gms. to 2500 ml. of water. Iron Solution: Dissolve .4474 gms. of ferric sulphate c.p. in 250 ml. of water, adding a few drops of sulfuric acid to dissolve basic salts.

[25] The above colorimetric method is by Mr. S. Skowronski, Research Chemist, Raritan Copper Works.

Determination of Bismuth in Wire Bar Copper [27]

A 100 gram sample is dissolved in a 2500 ml. beaker with 400 ml. of nitric acid (1.42) and 300 ml. water. When all is in solution, add one half gram of calcium carbonate, dilute to 1500 ml. and boil. Cautiously add ammonia (1:1) until all basic salts are dissolved, boil and add four cubes of ammonium carbonate.

Let settle about 30 minutes or longer. Filter on a 1" Hirsch filter plate covered with asbestos, using suction; wash with dilute ammonia containing ammonium carbonate until the precipitate appears to be copper-free.

Dissolve the precipitate off the pad with nitric acid (1:1), dilute to 150 ml., make ammoniacal, boil and re-precipitate with two cubes of ammonium carbonate.

Allow to settle at least 30 minutes, and filter as before. Dissolve the precipitate off the pad with 2 ml. of nitric acid and in 10 ml. of water, wash, keeping the volume below 50 ml.

Transfer to a Nessler tube, add 1 ml. of saturated SO_2 water, and 5 ml. of 30% potassium iodide solution, match the color in a standard tube containing 2 ml. of HNO_3 in 50 ml. of water, 1 ml. of SO_2 water and 5 ml. of 30% KI solution.

Add standard bismuth solution till the color of one tube matches the other.

Standard Bismuth Solution.—1 ml. equals .0001 gram of bismuth. Dissolve .1 gram of bismuth in 10 ml. of nitric acid and make up to a liter.

NOTES.—Bismuth carbonate comes down with the calcium carbonate in the same manner as lead carbonate.

Small quantities of lead do not interfere, lead nitrate does not color a potassium iodide solution, if present in large quantities an insoluble lead iodide is formed, which may be filtered off. Large amounts of lead iodide may carry some bismuth.

Copper and iron interfere and should be removed. Copper is removed by the double precipitation and the effect of traces of iron is neutralized by the addition of SO_2 water.

The addition of 1 ml. of saturated SO_2 water is essential to remove any free iodine which may be liberated. SO_2 in itself gives a slight color, which is compensated by addition of same amount to both tubes.

The addition of an excess of acid will liberate iodine and give a color. 2 ml. of nitric acid (1.42) in 50 ml. of water will not decompose KI. The same amount should be used in both tubes.

After the determination, it is well to add starch solution to both tubes, any indication of free iodine other than slight blue color, renders the determination worthless.

The method is only accurate for traces of bismuth. .0001 gram of bismuth can easily be detected, and bismuth should not be present in a greater quantity than .002 gram.

The method has been tested with known samples, with success.

DETERMINATION OF ZINC, NICKEL, AND COBALT

Removal of Copper.—Ten to 25 grams of blister copper, and 100 to 250 grams of refined copper in 25-gram portions are taken for analysis. The metal is dissolved in nitric acid (40 ml. per 10 grams) and the solution boiled until a faint green precipitate begins to appear on the surface of the solution. The free acid being expelled, the solution is made faintly acid by adding 1 to 2 ml. of nitric acid, the solution diluted 300 to 700 ml., according to the amount

[27] Method furnished by S. Skowronski, Research Chemist, Raritan Copper Works.

of copper taken, and then electrolyzed with a current of 1.5 to 2 amperes for thirty-six hours, with a spiral anode and a cathode with about 160 sq. cm. depositing surface. The solution should remain slightly acid throughout the electrolysis, otherwise cobalt, nickel, and zinc may be precipitated as hydroxides from a neutral solution. When the copper is nearly removed, the electrodes are disconnected, and removed.

The solution is concentrated by boiling, a few crystals of oxalic acid added, and the anode (which may be coated with PbO_2) immersed in the hot solution for a few minutes, then rinsed off into the solution.

Separation of Lead.—The solution is evaporated to small volume, about 40 ml. of dilute sulfuric acid (1 : 1) are added and the mixture evaporated to SO_3 fumes. The cooled concentrate is diluted with 100 ml. of water and again evaporated to fumes. About 300 ml. of water are added and when the soluble salts have dissolved, the solution is filtered and the residue, $PbSO_4$, washed. The filtrate contains Zn, Ni, Co, etc.

Removal of the Hydrogen Sulfide Group.—The filtrate from the lead sulfate is saturated with H_2S and filtered. The filtrate contains zinc, cobalt, and nickel. To recover any occluded zinc, the precipitate is dissolved in nitric acid, taken to fumes with sulfuric acid, diluted to about 200 ml., and again treated with H_2S. The filtrate from this precipitate is combined with the first portion. The precipitate is rejected.

Removal of Iron.—This, if present, will be found in the filtrate. The H_2S is expelled by boiling and the solution concentrated to 400 ml. after adding 5 ml. of H_2O_2 to oxidize the iron. Five grams of ammonium sulfate are added, the solution made strongly ammoniacal, and filtered. Iron is precipitated as $Fe(OH)_3$ and is thus removed. If much iron is present, a double precipitation is advisable to recover any occluded zinc, nickel, or cobalt, and the filtrates combined.

Determination of Zinc.—The filtrate from iron is concentrated to 400 ml., then made neutral to litmus by cautious addition of dilute sulfuric acid, drop by drop, and then faintly acid with 3 drops in excess. Zinc is now precipitated as the sulfide by saturating the solution with H_2S and allowing to stand over night. The sulfide is filtered off. The filtrate contains cobalt and nickel.

Zinc sulfide is dissolved in hot dilute HCl (1 : 2) and a few crystals of $KClO_3$. The solution is evaporated to dryness, the residue taken up with water containing a few drops of HCl and the extract filtered (to remove any SiO_2 dissolved from the beakers). Zinc carbonate is now precipitated (in a beaker of glass, which does not contain zinc) from the filtrate by addition of sodium carbonate, and ignited to the oxide ZnO.

$$ZnO \times 0.8034 = Zn.$$

Determination of Nickel and Cobalt.—The filtrate from the zinc sulfide is examined for nickel and cobalt. About 0.5 ml. of sulfuric acid is added. H_2S is expelled by boiling, and 2 ml. of H_2O_2 added. The solution is concentrated to about 400 ml. (this should be free from nitric acid), treated with about 25 ml. of ammonium hydroxide, and electrolyzed over night with a current of 0.5 ampere. Nickel and cobalt, if present, are deposited on the cathode as metals

and so determined. For greater details, consult the chapter on Nickel under the method by electrolysis.

DETERMINATION OF LEAD—MODIFICATION OF SKOWRONSKI METHOD

For blister copper use a 50 g. sample and 100 g. for refined copper.

Dissolve the copper in a 1500 ml. beaker. For each 50 g. add 75 ml. of water and 200 ml. of concentrated HNO_3.

When solution of the copper is complete, add 5 g. of powdered calcium carbonate and then 600 ml. of NH_4OH. Bring to boiling on a hot plate and add 150 ml. of a saturated solution of $(NH_4)_2CO_3$ and remove to a steam plate.

Allow to settle for 45 minutes. Filter [28] through a 15 cm. fine filter paper. Wash as free as possible of copper. Wash the precipitate from the paper back into the original beaker.

Dissolve precipitate in 10 ml. of conc. HNO_3. Evaporate to dryness and bake on a hot plate. When a considerable quantity of iron is present, it is necessary to bake until the Fe_2O_3 is rendered insoluble in acetic acid.

Remove from the hot plate, cool, and add 10 ml. of acetic acid and 100 ml. of water. Boil for a few minutes and filter through a fine paper. Wash the paper four times with hot water. Add distilled water to bring the volume to 200 ml. Bring to boiling and add a saturated solution of potassium bichromate in sufficient quantity to precipitate the lead. Refined copper requires a maximum of 5 ml. of this precipitant.

Boil for ten minutes, remove from the hot plate and allow to stand overnight at room temperature.

Filter on a weighed filter crucible, dry for one hour at 100° C. Cool and weigh.

$$PbCrO_4 \times .641 = Pb$$

DETERMINATION OF ARSENIC, ANTIMONY, SELENIUM, AND TELLURIUM

Separation of Copper.—Ten to 50 grams of blister copper and 100 to 500 grams of refined copper are required for the determination. (For 500-gram sample, 5 lots of 100 grams are taken.) The drillings are dissolved in nitric acid (40 ml. per 10 grams) and the solution boiled until a light-green precipitate appears on the surface. The liquor is diluted to 500 ml., and 5 ml. of ferric nitrate containing 3% of iron are added. A basic acetate precipitate is now made, weak sodium carbonate solution being added to neutralize the free acid, but not in sufficient amount to produce a permanent precipitate. If the endpoint is overrun, nitric acid is added drop by drop until the solution clears. The solution is diluted to about 800 ml., 20 ml. of a saturated solution of sodium acetate added, the liquor brought to boiling and filtered hot through a large creased filter paper, the first portion of the filtrate being poured back on the

[28] In the case of refined copper most of the supernatant solution may be decanted into the sink, because the quantity of lead is very small and the calcium carbonate precipitate, carrying the $PbCO_3$, settles very well.

filter. The residue is washed twice with hot water to remove the copper. Five ml. additional iron are added to the filtrate and a second basic acetate precipitation made, a separate filter being used. The precipitates are dissolved in the least amount of nitric acid necessary and the solutions combined. The liquor is concentrated to 150 ml., a pinch of potassium chlorate added, and the concentration continued until the volume has been reduced to about 30 ml. An equal volume of conc. hydrochloric acid is added and a second pinch of chlorate and the evaporation repeated to eliminate all traces of nitric acid.

The evaporation is best conducted in a casserole, resting in the circular opening of an asbestos board, in order that the sides of the vessel may be protected from the flame.

Separation and Determination of Arsenic.—The solution is transferred to a distillation flask, arsenic reduced with ferrous chloride, and distilled according to the standard procedure for this element, p. 91.[29] In this distillate arsenic is determined volumetrically.[30] (See chapter on Arsenic.) Antimony, selenium and tellurium remain in the flask.

Separation and Determination of Antimony.—Twenty-five ml. of a saturated solution of zinc chloride are added to the liquor remaining in the distilling flask after the elimination of arsenic. The antimony is now distilled, conc. hydrochloric acid being introduced in the distilling flask drop by drop by means of a separatory funnel, to replace the solution distilled, the volume in the flask being kept as low as possible, avoiding crystallization.

The antimony is determined by the potassium bromate titration method, as described in the chapter on Antimony. Small amounts of Se, Te, Fe^{+++}, Cu and Sn do not interfere with the potassium bromate titration.

Alternative Method.—Electrolytic Determination of Sb.[31] The distillate is neutralized with ammonia, then made slightly acid with HCl and the antimony is precipitated with H_2S, and filtered.

The precipitate is dissolved in dilute HCl (1 : 2), containing a little bromine to oxidize the sulfur. The solution is filtered free from sulfur and the filter washed with a little dilute HCl. The filtrate should contain one-third its volume of conc. HCl. Selenium is now precipitated by passing in SO_2 gas to saturation and bringing the solution to boiling. The precipitate is allowed to settle several hours and then filtered through a fine filter. The filtrate contains antimony.

After boiling out the SO_2, the filtrate is first neutralized with ammonia, then made slightly acid with hydrochloric acid and antimony precipitated as the sulfide by saturating the solution with H_2S, allowing the precipitate to settle, resaturating with H_2S and again allowing to settle. The filtered, washed precipitate is dissolved with sodium sulfide, and 10 ml. of 25% potassium cyanide (poison) added to the filtrate, together with 2 ml. of 25% sodium hydroxide.

The solution is now electrolyzed hot (90° C.) for an hour with a current of 0.5 ampere and antimony deposited as the metal on the cathode. This is

[29] The concentration should not be carried below 30 ml.

[30] Arsenic may be precipitated by H_2S, the sulfide dissolved in NH_4OH, the filtrate taken to dryness, HNO_3 added and the evaporation repeated. Arsenic now is determined by precipitation with $AgNO_3$ and titration of the silver with KCNS in presence of a ferric salt. $Ag \times 0.2318 = As$.

[31] This procedure has been largely abandoned in favor of the bromate titration.

quickly removed and washed by dipping it successively into a beaker of cold water, three of hot water and one of 95% alcohol. The cathode is dried at 100° C., and then weighed, on cooling, as usual. *Antimony* is now removed by immersing the cathode in boiling nitric acid containing tartaric acid, and washing as before. The loss of weight of the foil is taken as antimony.

NOTE.—It is advisable to test the electrolyte for antimony by acidifying the solution with oxalic acid (Hood). A reddish coloration indicates the incomplete removal of the element.

SELENIUM AND TELLURIUM

50 g. of blister copper used.
100 g. of refined copper used.

Dissolve the copper in nitric acid, boil until a light green precipitate appears on the surface. Dilute to 500 ml. for each 50 g. of copper and add 5 ml. of ferric nitrate, containing 3% of iron (to each 50 gm. portion). Make the basic acetate separation as described in the arsenic and antimony method.

Dissolve the iron precipitate in HCl. Add about 5 g. of $KClO_3$ (crystals). Evaporate to 20 ml. Add 20 ml. H_2O. Cool and filter through fine paper to remove the insoluble precipitate and paper fibre. Wash several times with cold distilled water, keeping the volume down to 150 ml.

Add 20 ml. concentrated hydrochloric acid and pass SO_2 gas through solution for 10 minutes, thus precipitating tellurium. Heat gently to just below the boiling point, when 40 ml. HCl are added to precipitate selenium.

Pass SO_2 for 10 minutes longer. Allow to stand at least six hours and filter through a previously tared and ignited Gooch crucible. Wash five times with hot water and finally with alcohol. (The Gooch crucible which contains an Asbestos mat should be treated with a solution of hydrochloric acid of the same strength as the test, and saturated with SO_2, before the initial ignition and weighing.) Dry at 100° C. for one hour. Cool in desiccator and weigh.

$$\frac{\text{Weight of Se and Te} \times 100}{\text{Weight of sample}} = \%\ \text{Se and Te}$$

The precipitate of Se and Te may contain gold, which must be determined by cupellation assay.

The following colorimetric method is very accurate for selenium alone in minute amounts such as found in refined copper.

The combined Se and Te, as found above are dissolved through the filter in about 15 ml. of hydrochloric acid—bromine mixture. Wash the filter twice with minimum of water. Heat this solution at 70° C. until bromine has been expelled. Cool and add 1 ml. of conc. H_2SO_4 and evaporate to conc. H_2SO_4 at temperature below 100° C.

Add 1 ml. to 2 ml. of water and 20 ml. of conc. hydrochloric acid saturated with SO_2. Transfer to test tube or comparison tube.

Prepare another test tube for comparison with an equal quantity of each reagent used above. To this tube add slowly a standard solution of selenious acid, weakly acidified with HCl, until the depth of color matches the test.

Standard Selenious Acid Solution.—Dissolve .500 gm. of pure selenium in 10 ml. of conc. HNO_3. Evaporate to dryness on steam plate. Make two

additions of 20 ml. each of conc. HCl to expel nitrates. Each time evaporate to about 3 or 4 ml. If it is allowed to go to dryness there is danger of loss of selenium.

Finally take up with 50 ml. of 1 : 1 hydrochloric acid and make up to 1000 ml. *with distilled* H_2O.

DETERMINATION OF OXYGEN

This determination is required only in refined copper. The method depends upon the reduction with hydrogen of cuprous oxide heated to redness, the water formed by the reaction being the measure of the oxygen.

Apparatus.—The combustion-furnace is the same as that used for the determination of carbon. As it is necessary that the hydrogen be absolutely free from oxygen and moisture, the gas is passed through a preheater consisting of a platinum or silica tube of small bore heated to redness by a flame or an electrical device. The gas is then passed through a tube containing calcium chloride and finally through a P_2O_5 bulb containing the anhydride. In this purified form it enters the combustion-tube. The product of combustion, water, is absorbed in a tared bulb by P_2O_5, to which is attached a tube of calcium chloride.

Procedure.—The sample, which has been drilled with considerable care to avoid overheating, is dried under partial vacuum in a desiccator after warming to below 70° C. for a few minutes.

One hundred grams are taken for analysis and placed in the combustion tube, the drillings being held in a large boat. Purified hydrogen is rapidly passed through the tube for half an hour to sweep out the air, the tube being cold. The tared P_2O_5 bulb and the calcium chloride tube are now attached. The heat is turned on to bring the sample to cherry red heat, 900° C., and the current of hydrogen passed slowly over the sample for several hours.

The increase of weight of the P_2O_5 bulb $= H_2O$.

$$H_2O \times 0.8881 = O. \quad O \times 4.9687 = CuO.$$

DETERMINATION OF SULFUR

This determination is rarely required in refined copper.

Twenty grams of blister, unrefined or cement copper, placed in a casserole, are treated cold with 50 ml. bromine-potassium bromide mixture (see under Determination of Selenium and Tellurium). After standing at least ten minutes, 100 ml. of strong nitric acid are added. After another ten minutes the casserole is placed on the steam bath and the solution evaporated to small volume. This is taken up with 25 ml. of conc. hydrochloric acid and evaporated to a pasty mass. The treatment is repeated to ensure the decomposition of nitrates and to expel nitric acid. It is now taken up with 5 ml. of hydrochloric acid, diluted with water and sulfuric acid precipitated as $BaSO_4$, according to the standard procedure for sulfur.

$$BaSO_4 \times 0.13735 = S.$$

DETERMINATION OF PHOSPHORUS

This determination is seldom required, and then only in low-grade copper and copper scrap containing phosphor bronze. The sample, dissolved in nitric acid, is treated with ferric nitrate and the basic acetate precipitation made as has been described for the determination of arsenic, etc. The precipitate is dissolved in HCl, this solution then made strongly ammoniacal, and saturated with H_2S, and filtered. The filtrate containing the arsenic and phosphoric acid is acidified, arsenic sulfide and sulfur filtered off, and phosphoric acid determined in the filtrate by precipitation with magnesia mixture as usual. See chapter on Phosphorus.

$$Mg_2P_2O_7 \times .2786 = P.$$

DETERMINATION OF COPPER IN REFINED COPPER

In determining the quality of copper for electrical purposes each hundredth of a per cent above 99.90 has its significance. The methods employed are the electrolytic and the hydrogen reduction methods. Silver present is rated as copper.

Electrolytic Method.[32]—The sample, consisting of unground drillings, should be untarnished, free of grease or oil, and cleaned of particles of iron by use of a good magnet.

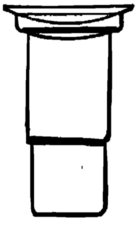


FIG. 45. Special Beaker for Electrolysis of Copper.

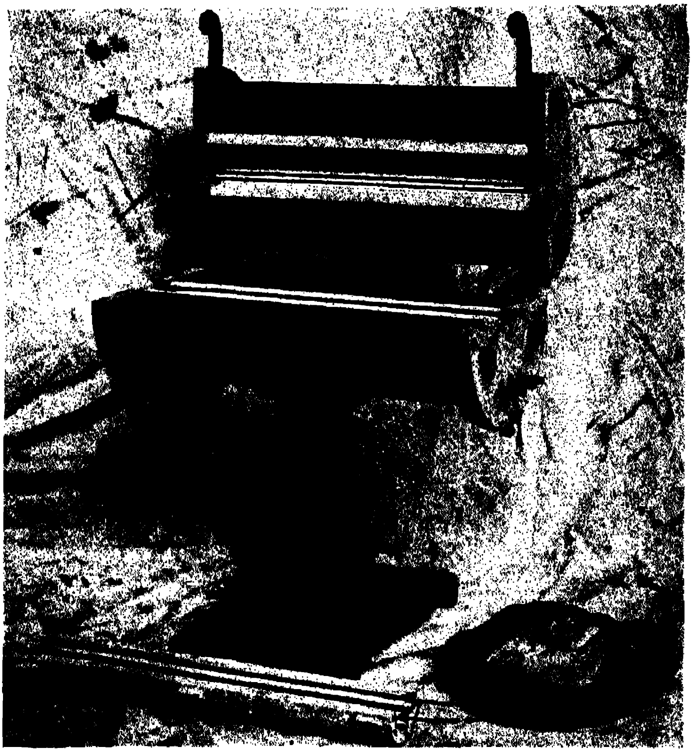
Procedure.—A catch weight of about 5 grams is taken, each piece being examined for dust, particles from the drill and surface oxidation before it is placed on the balance pan. Solution is effected in a special 400-ml. beaker which has hipped sides to support a series of watch glasses, the lower hip at the 125 ml. mark, the upper at 350 ml. (Fig. 45).

The drillings are treated with 50 ml. of a stock solution (10.5 parts nitric acid and 4.5 parts of sulfuric). The watch-glass traps are put in place to retain the copper, which is always entrained in the nitrogen peroxide fumes. Except that the current is maintained at .75 ampere throughout the period of electrolysis, the conditions are the same as have been described for the determination of copper by the "Small Portion Method."

Hydrogen Reduction Method.—This method is applicable to the determination of copper in grades of refined copper which are characterized by a metallic impurity content which is constant and less than 0.01%. The apparatus

[32] Ferguson, J. Ind. Eng. Chem., 2, 187 (1910).

consists of a combustion furnace, preferably electrically heated, the temperature of which can be kept constant at about 950° C.; a silica tube of ¾-in. bore, one end of which is connected with a large Peligot tube containing



By courtesy of the Hevi-Duty Electric Co., New York City.

FIG. 46.—Combustion Furnace, Hinged Design, Type 70—Shown with One "Spare" Unit. Height to center, 9½".

concentrated sulfuric acid, the other end is connected by a rubber plug and flexible tube with a source of purified hydrogen. Porcelain combustion boats 95 mm. long, 18 mm. wide and 10 mm. deep are used.

Procedure.—A catch weight of about 25.1 grams of drillings is placed in the combustion boat, and the boat inserted in the silica tube. After passing hydrogen for half an hour through the cold tube, the temperature is raised to 950° C. and so maintained for two hours. If the furnace is of a type which will permit the removal of the tube without disconnecting the train,[33] the tube is taken from the furnace without interruption of the stream of hydrogen and cooled by a jet of cold air. When cold, the mass of copper, the particles of which are cemented, is taken from the boat and weighed.

NOTE.—If the sample is allowed to become molten, the boat and tube will be coated with a film of copper.

A convenient and efficient type of combustion furnace, hinged design, is shown in Fig. 46. This furnace may be purchased from the Hevi-Duty Electric Co., New York City.

[33] Hevi-Duty Electric Co., New York.

CHLORINE IN CEMENT COPPER AND COPPER ORES

If the material contains very little silver the following method is applicable in laboratories equipped with apparatus for furnace assaying.

Ten grams of the finely ground sample placed in an 800-ml. beaker are treated with 600 ml. water, 100 ml. nitric acid (free from iodic acid) and the mixture brought to boiling by gentle heating. After filtration and thorough washing, the insoluble residue is treated repeatedly with additional water and acid, of the above proportion, until a test of the filtrate with silver nitrate indicates complete extraction of the soluble chloride. The combined filtrates are treated with a slight excess of silver nitrate and chloride of silver precipitated and determined in the usual way.

On a separate 10-gram sample an assay of silver is made and the equivalent weight of chloride calculated. This equivalent is added to the weight of silver chloride obtained in the extract. The per cent of chlorine is calculated from this result by the formula

$$\frac{\text{Weight of AgCl} \times .2474 \times 100}{10} = \text{Per cent chlorine.}$$

DETERMINATION OF COPPER IN BLUE VITRIOL

This is best determined on a 2-gram sample of the finely powdered dry salt or a catch weight of approximately 2 grams if the salt is moist. Copper is deposited electrolytically, the electrolyte being diluted to 130 ml. and containing 4 ml. of nitric acid and 5 ml. saturated solution of ammonium nitrate. A current of .18 ampere and an electrode of $11\frac{1}{2}$ sq. in. depositing surface are used. If the salt contains insoluble matter consisting wholly of basic salts, complete solution is brought about by gently boiling after adding 4 ml. nitric acid and 25 ml. of hot water to the salt. If the insoluble matter shows a tendency to remain in suspension, the presence of arsenic or antimony is indicated. In this case the impurities are precipitated along with ferric hydroxide, as has been previously described under the notes on the electrolytic determination of copper in blister copper.

DETERMINATION OF COPPER AND LEAD IN BRASS [34]

One gram of the alloy is dissolved in 8 ml. nitric acid and the nitrous fumes are boiled off; if tin is present, 40 ml. of boiling water are added, the metastannic

[34] Method of The National Brass and Copper Tube Company, communication by R. T. Roberts.

acid allowed to settle on the hot plate for fifteen minutes and filtered off. (Method for tin is accurate only for wrought brass; high iron or antimony interferes.)

The filtrate from the tin is electrolyzed for copper and lead. If the lead is less than 0.75%, an ordinary sandblasted, spiral anode is used; if the amount of lead is 0.75 to 5%, a sandblasted gauze cylinder is necessary. For amounts of lead over 5% either a smaller sample is taken or the greater part of the lead is precipitated as lead sulfate and the small amount of lead passing into the filtrate is recovered by electrolysis, using $\frac{1}{4}$ ampere current per solution, after adding 3 ml. of nitric acid. For lead under 0.5%, 5 ml. of (1 : 1) sulfuric acid are stirred in, after the current has been passing for at least ten minutes. If the lead is high the sulfuric acid is added after the electrolysis has continued for at least an hour. Under these conditions no lead sulfate deposits from the solution and as long as the current passes, the sulfuric acid present does not attack the PbO_2 deposited. After the sulfuric acid is added the current is raised to $\frac{1}{2}$ ampere per solution and the electrolysis continued overnight.

The lead peroxide is dried at 250° C. for half an hour. The factor 86.62 gives the equivalent per cent lead. (Factor determined from the average of a large number of tests made on pure lead. The factor is best obtained under the conditions of the laboratory where the determinations are made, as it varies slightly with change of conditions.)

The copper on the cathode is washed, dried and weighed according to the usual standard procedure.

METHODS OF DETERMINING THE COMBINATIONS OF COPPER IN ORES AND FURNACE PRODUCTS

SULFUROUS ACID METHOD[35]

The method is based on results which show that cuprite, melaconite, malachite, chrysocolla, and metallic copper, when finely pulverized, are readily and completely soluble in sulfurous acid. Copper sulfides, chalcocite and chalcopyrite, are not attacked, no matter how finely pulverized or how long the period of contact. Metallic iron in quantities ordinarily found in pulverized mineral, even up to 3%, dissolves and affects the determination not at all, provided there is a strong excess of H_2SO_3. The essential conditions of the method are: (*a*) Fine pulverization of the sample in order to completely liberate the particles of copper minerals from the gangue; (*b*) the powdered sample must be kept in suspension during the period of lixiviation. Most ores give recovery in a half hour's contact and refractory ores yield in less than two hours.

In general, a solution containing 3% SO_2 should be used, but a much weaker one, as low as 0.75%, will suffice in the case of some ores.

[35] Van Barneveld and Leaver, Chem. and Met. Eng., **18**, 204 (1918). Eng. and Mining J., **105**, 552 (1918).

NOTE.—For the manufacture of sulfurous acid, an absorption tower of 1 in. dia. and 4 ft. long glass tubing filled with broken hard-burned fire clay is set at an angle of 75° between two 3 to 5 gal. bottles, one about 5 ft. above the other. The tube is open at the top and sealed at the bottom with a plug of sealing wax, through which two small glass tubes extend. The upper bottle contains cold distilled water which is siphoned into the upper end of the absorption tower, the flow being regulated by a stopcock. A 6 to 50 lb. cylinder of sulfur dioxide is connected to one of the glass tubes extending into the absorption tower. On opening the valve of the cylinder the issuing SO_2 is gasified and passes to the tower where it is absorbed by water from the upper bottle, converted into SO_2 solution of the desired strength and caught in the lower bottle. A gas generator may be employed instead of cylinder of SO_2. A 3% solution of SO_2 may be produced by this apparatus at the rate of 3 liters per hour.

The procedure is as follows: Place 2 grams of pulp of 100 to 150 mesh fineness in a bottle, add 100 ml. 3% solution of SO_2, seal the bottle and agitate by rolling ½ to 3 hours. Filter, wash the residue with SO_2 solution and add the washings to the filtrate which contains in solution all oxides, carbonates and silicates of copper and all the metallic copper. To this solution add 5 to 10 ml. nitric acid, evaporate to 20 ml., dilute with distilled water and determine copper by the electrolytic or other method suitable to the quantity.

The residue from the filtration contains the unaltered and undissolved sulfides, the copper in which is determined by the method suitable to the grade of ore.

THE SILVER SULFATE-SULFURIC METHOD [36]

The method as described is especially adapted to the determination of metallic copper, cuprous oxide and cupric oxide in the raw material used for the manufacture of marine paints, but can with obvious modifications be applied to the differentiation of sulfide and metallic from oxidized copper in ores. Particles of iron from the grinding plates do not interfere. The sample should be no coarser than 150 mesh.

According to the importance of close valuation of any constituent, 2, 5, or 10 grams of the sample are placed in an 800-ml. beaker together with 300 ml. of a neutral, saturated solution of silver sulfate. Boil gently for 10 minutes, decant the solution onto a 15 cm., thick filter paper of close texture and wash the residue in the beaker by decantation. These operations are repeated with addition each time of more silver sulfate, until a NH_4OH test of a filtrate shows no copper. When extraction of all metallic or sulfide copper has been accomplished, the entire residue is transferred to the filter and washed with hot water until an HCl test of the washing shows the presence of no silver. After evaporation to convenient volume and precipitation of silver from the hot liquid by dilute HCl (cautiously added to ensure no excess in case determination is to be by the electrolytic method), removal of the precipitate by filtration only after the liquid has become cold, copper is determined in the whole or an aliquot part by the electrolytic or iodide method.

The residue is washed (with care not to break the paper) into a beaker or flask and boiled for 5 minutes with 200 ml. of 10% H_2SO_4 to bring into solution all the copper combined as CuO and half that combined as Cu_2O. Decant the solution upon the filter used for the silver sulfate leach to decompose particles

[36] Communicated by E. F. Fitzpatrick, chemist, Nichols Copper Co.

of oxides which may be retained upon the paper. Wash thoroughly with cold water.

The copper on the filter, precipitated by the reaction $Cu_2O + H_2SO_4 = Cu + CuSO_4$, is dissolved with dilute nitric acid (sp.gr. 1.1). The solution filtered and freed from silver by the same method and with the same precautions as were employed on the filtrate from the treatment with 10% H_2SO_4. According to the amount of sample taken or the evident quantity of copper in solution, copper is determined, by any method suitable to the quantity, in the whole or an aliquot part. This copper in terms of per cent content in the sample multiplied by two gives the copper combined as cuprous oxide, and multiplied by 1.1258 gives per cent Cu_2O.

From the per cent of copper in the sample dissolved by 10% H_2SO_4 and determined by any method suitable to the quantity is subtracted that precipitated by the same operation to obtain by difference copper combined as cupric oxide. This multiplied by 1.2517 gives the per cent CuO.

PHOSPHORIC ACID–AMMONIUM CHLORIDE METHOD[37]

This method depends upon the solubility of carbonates and silicates and insolubility of sulfides of copper in 15% phosphoric acid; also upon the solubility of metallic copper in a solution of ammonium chloride. Metallic iron does not interfere.

One gram of the fine sample is placed in a 500-ml. flat bottom flask, covered with 20 ml. of 15% H_3PO_4 and an equal amount of a 20% NH_4Cl solution and boiled gently for 10 minutes. Because H_3PO_4 gives to the solution a yellow tint which interferes with a sharp end-point in the determination of copper by the cyanide method, a pinch of burned lime is added to the solution after it has cooled somewhat. The flask is thoroughly shaken, 25 ml. strong ammonia added and the solution boiled again for some time. The ammoniacal copper solution is filtered from the residue, allowed to cool and titrated by the cyanide method. The method as described is adapted to ores containing up to 3% of oxidized copper.

CAUSTIC SODA–SODIUM TARTRATE METHOD[38]

This method is based on the permanence of sulfides, the rapid yielding to solution of cupric oxide and the decomposition of cuprous oxide ores on treatment with a mixture of caustic soda and sodium tartrate; also upon the solubility of the more refractory form of oxide of copper by a mixture of ammonium hydrate and sulfate. The method is subject to some error because washing with the ammonia solution dissolves some copper from the chalcocite, and because of the difficulty of washing out all of the dissolved copper from the gelatinized spongy mass on the filter when chrysocolla is a constituent of the sample. These errors tend to balance each other when chalcocite and chrysocolla are both present and the resultant error in assays of ores containing less than 5% copper is not serious.

[37] Cremer, Chem. and Met. Eng., 18, 644 (1918).
[38] Hunt and Thurston, Colo. School Mines Mag., 157 (1917).

The procedure is to add 20 ml. of a solution of sodium hydrate and tartrate to 2 grams of pulp and boil gently for 5 to 10 minutes with occasional shaking of the beaker. While hot add 25 ml. 20% solution of ammonium sulfate, heat for 10 minutes, filter, wash several times with a hot mixture of ammonium hydrate and sulfate and finish the washing with hot water. Neutralize the filtrate with dilute H_2SO_4, add 2½ ml. concentrated HNO_3 and determine copper by the electrolytic method.

NOTE.—The caustic soda-sodium hydrate stock solution consists of 100 grams sodium hydrate and 50 of sodium tartrate dissolved in 1000 ml. distilled water. The ammonium hydroxide and sulfate washing solution is a mixture of 100 ml. ammonium hydrate, 100 grams ammonium sulfate and 1000 ml. distilled water.

SULFURIC ACID–MERCURY METHOD [39]

This method depends upon the dissolution of oxide copper by dilute sulfuric acid and amalgamation of metallic copper, native and that resulting from the decomposition of cuprous oxide, thus separating intact sulfide copper.

According to the copper content, 1 to 3 grams of the sample are heated at 80° to 90° C. for 30 to 45 minutes in a 150-ml. casserole with 50 ml. of 4% H_2SO_4, care being taken to avoid boiling. Cool then to room temperature and add 4 to 5 ml. clean mercury. Rub the mercury about the casserole with glass rod or other object for 3 or 5 minutes until it is certain that all the particles of ore have come in contact with the mercury. Pour the supernatant solution containing the sulfide minerals suspended in it into a beaker, taking care to retain the mercury in a single globule in the casserole. Wash the last traces of the ore into the beaker by means of a fine stream of water. The solution is now filtered and the copper determined by any suitable method.

The copper in the residue represents the sulfide, while that in the filtrate represents the so-called " oxide " or sulfuric acid soluble copper.

DETERMINATION OF METALLIC COPPER IN MIXTURES CONTAINING CUPROUS AND CUPRIC OXIDE [40]

The method depends upon the solubility of cuprous oxide in cold aqueous ammonia, containing hydrazine sulfate in a CO_2 atmosphere. The copper and the cupric oxide do not dissolve under these conditions.

Apparatus.—The filter consists essentially of a 55-mm. filter tube of the type used for small Gooch crucibles. In the opening is placed a perforated porcelain button which is seated at right angles to the stem. An asbestos pad

[39] Maier, Eng. and Mining J., 105, 372 (1918).
[40] L. C. Hurd and A. R Clark, Ind. Eng. Chem., Anal. Ed. 8, 380 (1936).

is built up over the button and securely set by tamping with a glass rod. The filter must be packed in such a manner that the tube may be held in an inverted position without disloding either the disk or the pad. It has been found that a tube about 60×25 mm., with a stem of 110 mm., is a convenient size. A 20-mm. Gooch crucible button serves to support the asbestos pad.

Procedure.—A sample of suitable size is weighed out on a small watch-glass, and the glass and contents are placed in a dry, wide-mouthed 250-ml. Erlenmeyer flask. If the material is an electrolytic product low in copper, it is advisable to take a 1- to 2-gram sample. If it is from a " thermal process," the percentage of copper is usually large and a smaller sample will suffice. The air in the flask is displaced with carbon dioxide (15 to 20 cubic feet per hour) and 10 ml. of ethyl alcohol are added to dissolve any oil present in the sample. Without interrupting the flow of gas, 150 ml. of extraction solution 6 g. C.P. hydrazine sulfate per liter of ammonia, sp.gr. 0.90) are added. Any lumps of oxide are broken up with a stirring rod. Violent agitation should be avoided. The carbon dioxide inlet should be about 5 cm. (2 inches) above the surface of the liquid. The time required for complete solution of all cuprous oxide varies between 1 and 5 minutes, depending upon the amount and character of the sample under investigation.

When the cuprous oxide has completely dissolved, as evidenced by the total disappearance of red particles, the filter is connected to a suction and slowly lowered into the flask. As soon as the bulk of the solution is removed, the flask is rinsed with carbon dioxide-saturated water and the filtration and washing are continued. Five or six 100-ml. portions of wash water will suffice to remove all the original extraction solution containing the dissolved cuprous oxide. The filter is then disconnected and the pad and contents are pushed back into the flask with a glass rod. Fifteen milliliters of ferric chloride solution 150 g. $FeCl_3 \cdot 6H_2O$ and 300 ml. HCl, sp.gr. 1.20 plus 800 ml. water free of air and saturated with CO_2 are added and the flask is warmed to dissolve the cupric oxide-copper residue. When all particles have disappeared, the solution is cooled to below 40° C. and 10 ml. of phosphoric acid and 3 drops of diphenylamine sulfonate indicator [41] are added. Dichromate solution is run into the flask until the end point, a change from pea green to intense purple, is reached.

The result is calculated according to the following equation:

$$\frac{\text{N of } K_2Cr_2O_7 \times \text{ml.} \times 0.03179}{\text{wt. of sample}} \times 100 = \%\ \text{Cu}$$

The percentage of cuprous oxide in the sample may be determined by dissolving a 0.2-gram sample in ferric chloride and titrating the ferrous iron produced with potassium dichromate in the manner described. It is essential that solution of the sample be carried out in an atmosphere of carbon dioxide or other inert gas. From the volume of dichromate solution equivalent to both the cuprous oxide and copper, the true percentage of cuprous oxide in the

[41] 2 g. of barium diphenylamine sulfonate in 50 ml. of air-free water and 5 g. of sodium sulfate, diluted with 50 ml. of air-free water saturated with CO_2. The clear liquid is used as the indicator solution.

sample may be calculated according to the following equation:

$$\frac{Ml_{K_2Cr_2O_7} - \left(\frac{\%Cu \times \text{wt. of sample}}{3.179 \times N}\right) \times 0.07157 \times N}{\text{wt. of sample}} \times 100 = \%\ Cu_2O$$

The calculation of the result is simplified if the sample taken for the copper determination be a simple multiple of that used in the oxide analysis. In actual practice it has been found that a 1.000-gram sample for metallic copper and a 0.2000-gram sample for cuprous oxide are of convenient size. In this case, one-fifth of the volume of dichromate used in the determination of metallic copper is subtracted from the total titration of the smaller sample to give the volume of dichromate actually equivalent to the cuprous oxide in the sample.

COPPER IN BRASS—SHORT IODIDE METHOD

Determination of copper in brass may be accomplished by the short iodide method given on page 371. The tin should remain in the solution since the tin oxide carries down a small amount of copper, which would be lost if the tin were removed by filtration as is prescribed for wrought brass using the electrolytic method. The sample is brought into solution by dilute nitric acid (1 : 1), the factor weight 0.6357 requires about 10 ml. HNO_3 and 5 ml. conc. sulfuric acid are added and the sample evaporated to strong fumes. Any copper that may have been occluded by tin passes into solution upon dilution with water; lead will remain as a white precipitate, but does not interfere and should be left in the solution. Addition of bromine water is generally necessary, and in any case will do no harm, the bromine being subsequently removed by boiling the solution.

COPPER IN BABBITT METAL AND ALLOYS HIGH IN TIN—SHORT IODIDE METHOD

High tin alloys may be decomposed, generally, by conc. sulfuric acid. This prevents formation of tin oxide obtained by the nitric acid method. If much copper is present, dilute nitric acid decomposition must be used, since copper is more readily attacked by nitric acid. (Copper is attacked by conc. sulfuric acid, but is insoluble in dilute sulfuric acid or hydrochloric acid.) Tin oxide occludes copper, as has been stated under the iodide method for brass; treatment with sulfuric acid, as prescribed, frees any occluded copper. Since tin and lead do not interfere in the method, their removal is not necessary nor advisable.

A considerable portion of the original chapter was contributed by Wallace G. Derby, formerly Research Chemist, Nichols Copper Co. Mr. E. C. Fitzpatrick has served as advisory editor for the chapter in the present edition. Mr. S. Skrowonski, Research Chemist, Raritan Copper Works, has contributed methods which are acknowledged in the text.

FLUORINE [1]

F′, *at.wt.* 19.00; D (*air*) 1.31$^{15°}$, *sp.gr.* (1.11^{-187}); *m.p.* −223° C; *b.p.* −187° C.; *acids* HF, H_2SiF_6

Fluorine is not found free in nature. It occurs combined with calcium in the mineral fluorspar, CaF_2; in cryolite, Na_3AlFi; in apatite, $Ca_5(Cl, F)(PO_4)_3$. It is found more frequently in silicic than in ferric rocks, the amounts being usually less than 0.1%. It occurs together with phosphorus in all animal and vegetable tissues.

DETECTION

Fluorine is the most active element known, and is by far the most active of the halogens, displacing chlorine, bromine, and iodine from their combinations.

Etching Test.—The procedure depends upon the corrosive action of hydrofluoric acid on glass, the acid being liberated from fluorides by means of hot concentrated sulfuric acid. This test is applicable to fluorides that are decomposed by sulfuric acid. The reactions taking place may be represented as follows:

$$\text{I.}\quad CaF_2+H_2SO_4=CaSO_4+2HF.$$

$$\text{II.}\quad SiO_2+4HF=2H_2O+SiF_4.$$

The test may be carried out in the apparatus shown in the illustration, Fig. 47. A clear, polished glass plate 2 in. square, free from scratches, is warmed and molten wax allowed to flow over one side of the plate, the excess of wax being drained off. A small mark is made through the wax, exposing the surface of the plate, care being exercised not to scratch the glass. If the test is to be quantitative, the marks should be of uniform length and width. The powdered material is placed in a large platinum crucible (*B*) (a lead crucible will do); sufficient concentrated sulfuric acid is added to cover the sample. The plate (*D*) with the wax side down is placed over the crucible and pressed firmly down. To prevent the wax from melting, a condenser (*C*), with flowing water, cools the plate. An Erlenmeyer flask (*C*) is an effective and simple form of con-

[1] Although fluorspar has been known for hundreds of years (named fluorspar during the period of Agricola, 1529) the element was not isolated until comparatively recent times (Moissan, 1886). In combined form as hydrofluoric acid and its salts fluorine is used commercially—etching of glass, insecticide, bleaching, etc.

denser, though a metallic cylinder is a better conductor of heat. A little water placed on the plate makes better contact with the condenser. As a further protection a wide collar of asbestos board (E) may be placed as shown in the figure. In quantitative work, where a careful regulation of heat is necessary, the crucible is placed in a casserole with concentrated sulfuric acid or in a sand bath, containing a thermometer to register the temperature. The run is best conducted at a temperature of 200° C. (not over 210°—H_2SO_4 fumes). After an hour the wax is removed with hot water and the plate wiped clean, and examined by reflected light for etching. A test is positive when the mark can be seen from both sides of the glass. Breathing over the etched surface intensifies the mark.

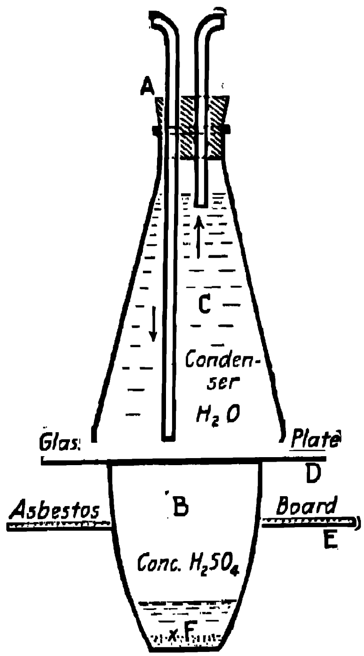


FIG. 47.—Etching Test for Fluorine.

Treatment of Fluosilicates not Attacked by Sulfuric Acid.—The powdered material is mixed with about eight times its weight of sodium carbonate and fused in a platinum crucible. The cooled melt is extracted with water. Calcium fluoride is thrown out from the filtrate, according to directions under Preparation and Solution of the Sample. The fluoride may now be tested as directed in the etching test or as follows by the hanging drop test.

The Hanging Drop Test.—The test depends upon the reaction $3SiF_4+3H_2O=2H_2SiF_6+H_2SiO_3$.

If the material contains carbonates, it is calcined to expel carbon dioxide. Half a gram of the powdered dry material is mixed with 0.1 gram dried precipitated silica and placed in a test-tube, Fig. 48, about 5 cm. long by 1 cm. in diameter. A one-hole rubber stopper fits in the tube. A short glass tube, closed at the upper end, passes through the stopper, extending about 3 mm. below. Two or three drops of water are placed in this small tube by means of a pipette, nearly filling it. Two ml. of concentrated sulfuric acid are added to the sample in the test-tube and this immediately closed by inserting the stopper carrying the hanging drop tube, exercising care to avoid dislodging the drop of water. The test-tube is placed in a beaker of boiling water and kept there for thirty minutes. If an appreciable quantity of fluorine is present a heavy gelatinous ring of silicic acid will be found at the end of the hanging drop tube in the stopper.

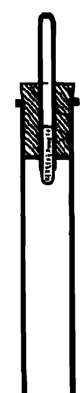


FIG. 48.—Hanging Drop Test for Fluorine.

It is important to have material, test-tube, and rubber stopper dry, so that the deposition may occur as stated.[2]

[2] C. D. Howard, J. Am. Chem. Soc., **28**, 1238 (1906).

NOTE.—Dr. Olsen[3] makes the test by heating the sample in a small Erlenmeyer flask, with concentrated sulfuric acid. A watch-crystal with a drop of water suspended on its curved surface is placed over the mouth of the flask. A spot etch is obtained in presence of fluorine.

Black Filter Paper Test.—According to Browning,[4] small amounts of fluorine may be detected by the converse method for detection of silicates and fluosilicates (see silicon). The fluoride is placed with a suitable amount of silica, in a small lead cup, 1 cm. in diameter and depth (Fig. 49); a few drops of concentrated sulfuric are added; the cup is covered by a flat piece of lead with a small hole in the center; upon the cover is placed a piece of moistened black filter paper and upon this a small pad of moistened filter paper. The cup is heated on the steam bath for ten or fifteen minutes.

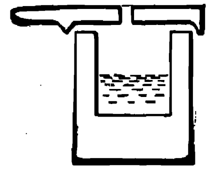


FIG. 49.—Black Filter Paper Test for Fluorine.

A white deposit will be found on the under side of the black filter paper, over the opening in the cover, if fluorine is present in an appreciable amount. (0.001 gram CaF_2 or above, and 0.005 gram Na_3AlF_6 will give the test.)

ESTIMATION

The determination of fluorine in the evaluation of minerals used for the production of hydrofluoric acid is of technical importance. The demand for elimination of the use of fluorides for preservatives of food makes its estimation in small amounts of importance.

Fluorine occurs only combined. It is found abundantly combined with lime in the mineral fluorspar, CaF_2. It occurs as cryolite, Na_3AlF_6; apatite, $Ca_4CaF(PO_4)_3$. It is found in mineral springs, ashes of plants, in bones, and in the teeth (CaF_2). It occurs sparingly, with aluminum and silicon, in topaz, and with cerium and yttrium in fluocerite, yttrocerite, also in wavellite, wagnerite, etc.

In the preparation of the material for analysis the volatility of silicon tetrafluoride should be borne in mind, and loss of HF in evaporations to fumes with sulfuric acid. In presence of calcium a loss of fluorine will occur by precipitation as CaF_2 with iron and aluminum when the solution is made ammoniacal. Accurate determinations of the element require considerable experience and much care to avoid loss and effect separations. The qualitative tests are simple.

[3] Communicated to the author by J. C. Olsen.

[4] P. E. Browning, Am. Jour. Sci. (4), 32, 249 (1910). "Methods in Chemical Analysis," by F. A. Gooch.

PREPARATION AND SOLUTION OF THE SAMPLE

Fluorides of the alkalies, and of silver and mercury, are readily soluble; copper, lead, zinc, and iron fluorides are sparingly soluble; the alkaline earth fluorides dissolve in 100 ml. H_2O as follows: $BaF_2 = 0.163$ gram, $SrF_2 = 0.012$ gram, $CaF_2 = 0.0016$ gram.

Fluosilicates of potassium, sodium, and barium are slightly soluble in water and practically insoluble if sufficient alcohol is added.

Organic Substances.[5]—These are best decomposed by the lime method, the details of which are given in the chapter on Chlorine under the section for the Preparation and Solution of the Sample, p. 263. For fluorides in organic matter it is advisable to decompose the substance in a seamless nickel tube, 40 mm. long by 4–5 mm. bore. The end of the tube is sealed with silver solder. The lime used should be soluble in acetic acid. The tube is heated to yellow heat for two hours. The lime is then extracted with acetic acid and fluorine determined as calcium fluoride.

Silicious Ores and Slags.—0.5 to 1.0 gram of material is fused in a crucible with ten times its weight of sodium and potassium carbonates (1 : 1) and poured into an iron mould. If a porcelain crucible has been used, this is broken up and added to the cooled fusion. The mass is digested with about 200 ml. of hot water for an hour, the mass having been broken up into small lumps, (Kneeland recommends using an agate-ware casserole as diminishing the liability of subsequent bumping),[6] then boiled briskly for ten minutes longer and filtered, the solution being caught in a large beaker. The residue is washed with hot water, followed by a hot solution of ammonium carbonate, and the insoluble material rejected. The silica is removed with ammonium carbonate, followed by the zinc oxide treatment of the second filtrate, as described under the section on Separations. In presence of appreciable amounts of fluorides, the gravimetric precipitation of fluorine as calcium fluoride is recommended.

Calcium Fluoride.—The product is best decomposed by fusion with sodium and potassium carbonates, after mixing the fluoride with 2.5 times as much silicic acid, followed by ten times its weight of carbonates. Most of the silicic acid and all the fluorine will be changed to soluble alkali salts, while the calcium will be left as insoluble calcium carbonate. The mixture must be heated gradually to prevent the contents of the crucible from running over by the rapid evolution of carbon dioxide. The thin liquid fusion soon thickens to a pasty mass. The reaction is complete when there is no further evolution of carbon dioxide. The fused mass is now extracted with hot water as indicated above, and the soluble fluoride filtered from the calcium carbonate residue. Silicic acid is removed from the filtrate by addition of ammonium carbonate. Traces of silicic acid are removed from the filtrate taken to near dryness, after neutralizing the alkali with dilute hydrochloric acid (phenolphthalein indicator), by the zinc oxide emulsion method given under Separations. Fluorine is precipitated as calcium fluoride, according to the procedure given later.

Soluble Fluorides.—See page 407.

[5] H. Meyer and A. Hub, Monatsh. Chem., 31, 933 (1910).
[6] E. Kneeland, Eng. and Mining J., 80, 1212 (1906). A. H. Low, "Technical Methods of Ore Analysis."

Hydrofluoric Acid.—See Vol. II, Acids.

Valuation of Fluorspar. Perchloric Acid Method.—One gram of fluorspar is treated with 15 ml. perchloric acid and 15 ml. of water in a suitable distillation flask and heated in an oil bath until the residue is almost dry. The distillation is continued with 10 ml. and finally 5 ml. portions of perchloric acid and equal amounts of water. Hydrofluoric acid may be determined as lead chlorofluoride in the distillate and water soluble residue analyzed for metals. If a residue analysis is desired treat first with HF, evaporate, and follow with perchloric acid. The residue is soluble in water or dilute HCl.

SEPARATIONS

Removal of Silicic Acid from Fluorides.—This separation is frequently required, especially in samples where the sodium and potassium carbonate fusion has been required for decomposition of fluosilicates, or calcium fluoride mixed with silicic acid. (See Preparation and Solution of the Sample.)

To the alkaline solution about 5 to 10 grams of ammonium carbonate are added, the solution boiled for five minutes and allowed to stand in the cold for two or three hours. (Treadwell and Hall recommend heating to 40° C., and allowing to stand over night.) The precipitate is filtered off and washed with ammonium carbonate solution. The fluoride passes into the filtrate, while practically all of the silicic acid remains on the filter.

Small amounts of silica in the filtrate are removed by evaporating the solution to near dryness on the water bath, then neutralizing the carbonate with dilute hydrochloric acid (phenolphthalein indicator) added to the residue taken up with a little water. Upon boiling the pink color is restored, the solution then cooled and acid again added to discharge the color; this is repeated until finally the addition of 1–2 ml. of 2 N HCl is sufficient to discharge the color. Four to 5 ml. of ammoniacal zinc oxide solution (moist ZnO dissolved in NH_4OH—Low recommends 20 ml. of an emulsion of ZnO in NH_4OH) is added and the mixture boiled until ammonia has been completely expelled. The precipitate of zinc silicate and oxide is filtered and washed with water. The fluoride is determined in the filtrate by precipitation with calcium chloride as directed later.

Separation of Hydrofluoric and Phosphoric Acids.—The method of Rose, modified by Treadwell and Koch,[7] takes advantage of the fact that silver phosphate is insoluble in water, whereas silver fluoride is soluble. The alkaline solution of the salts of the acids (solution of the sodium carbonate fusions) is carefully neutralized with nitric acid and transferred to a 300-ml. calibrated flask. A slight excess of silver nitrate solution is added, and the mixture made to volume and thoroughly shaken. After settling, the solution is filtered through a dry filter, the first 10 to 15 ml. being rejected; 225 ml. of this filtrate is again transferred to a 300-ml. calibrated flask, the excess of silver precipitated by adding sodium chloride solution, and after diluting to the mark and shaking, the precipitate is again allowed to settle; 200 ml. of this solution is taken for analysis, after filtering as previously directed. This sample represents 50% of

[7] Z. anal. Chem., 43, 469, 1904. "Analytical Chemistry," Vol. 2, by Treadwell and Hall. John Wiley and Sons.

the original sample taken. Fluorine is now determined by one of the procedures outlined.

Separation of Hydrofluoric and Hydrochloric Acids.—The solution containing hydrofluoric and hydrochloric acids, in a platinum dish, is treated with nitric acid and silver nitrate. The chloride is precipitated as the silver salt, whereas the fluorine remains in solution and may be filtered off through a glass funnel coated with paraffine or wax, or a hard rubber funnel. In presence of phosphoric acid, silver nitrate added to the solution will precipitate the phosphate as well as the chloride, whereas the fluoride remains in solution. The phosphate may be dissolved out from the chloride by means of dilute nitric acid.

Separation of Hydrofluoric and Boric Acids.—An excess of calcium chloride is added to the boiling alkali salt solutions of the two acids. The precipitate is filtered off and washed with hot water. The residue, consisting of calcium fluoride, borate and carbonate, is gently ignited and then treated with dilute acetic acid, taken to dryness, and the residue taken up with acetic acid and water. Calcium acetate and borate are dissolved, whereas the fluoride remains insoluble and may be filtered off and determined.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF FLUORINE

PRECIPITATION AS CALCIUM FLUORIDE

The method utilizes the insolubility of calcium fluoride in dilute acetic acid in its separation from calcium carbonate, the presence of which facilitates filtration of the slimy fluoride. The reaction for precipitation is as follows:

$$2NaF + CaCl_2 = CaF_2 + 2NaCl.$$

Procedure.—Solution of the sample and the removal of silica having been accomplished according to procedures given under Preparation and Solution of the Sample, and Separations, the solution is neutralized, if acid, by the addition of sodium carbonate in slight excess; if basic, by addition of hydrochloric acid in excess, followed by sodium carbonate. To this solution, faintly basic, 1 ml. of twice normal sodium carbonate reagent is added, followed by sufficient calcium chloride solution to precipitate completely the fluoride and the excess of carbonate, i.e., until no more precipitate forms, and then 2–3 ml. in excess. After the precipitate has settled, it is filtered and washed with hot water. (The filtrate should be tested for fluoride and carbonate with additional calcium chloride.) The precipitate of calcium fluoride and carbonate is dried

and transferred to a platinum dish, the ash of the filter, burned separately, is added and the material ignited. After cooling, an excess of dilute acetic acid is added, and the mixture evaporated to dryness on the water bath. The lime is converted to calcium acetate, while the fluoride remains unaffected. The residue is taken up with a little water, filtered and washed with small portions of hot water, by which procedure calcium acetate is removed, while calcium fluoride remains on the filter.[8] The residue is dried, separated from the filter and ignited. This, together with the ash of the filter, is weighed as calcium fluoride, CaF_2.

To confirm the result, the residue is treated with a slight excess of sulfuric acid and taken to fumes in a platinum dish. The adhering acid is removed as usual by heating with ammonium carbonate, and the ignited residue weighed as calcium sulfate. One gram of calcium fluoride should yield 1.7436 grams of calcium sulfate.[9]

$$CaO \times 1.3923 = CaF_2, \text{ or } \times 0.6776 = F.$$

Factors. $CaF_2 \times 0.4867 = F$, or $\times 0.5125 = HF$, or $\times 1.0758 = NaF$. $CaSO_4 \times 0.5735 = CaF_2$.

PRECIPITATION OF FLUORINE AS LEAD CHLOROFLUORIDE[10]

This method[11] is applicable to rather simple,[12] soluble and neutral fluorides. It precipitates granular and easily filtered PbFCl using hydrochloric acid and lead acetate. The precipitate is ideal, being about fourteen times heavier than the fluorine which it contains, but since it is quite soluble in water[13] a solution of PbFCl must be used for washing. The method is quite rapid and convenient. Its accuracy varies with the amount of fluorine present.[14] It has been used, with modification in the analysis of simple fluorides, electrolytic solutions,[15] enamels, paints, glasses,[16] and simple minerals.

Reagents.—Lead acetate. Ten per cent lead acetate solution containing 1% of glacial acetic acid.

Wash Solution.—Saturated PbFCl solution for washing precipitate.

NOTES.—Preparation of Wash Solution.
Part 1—Ten grams $Pb(NO_3)_2$ dissolved in 20 ml. H_2O.

[8] The results are slightly low, owing to the solubility of calcium fluoride: 100 ml. H_2O dissolves 0.0016 gram CaF_2; 100 ml. 1.5 N $HC_2H_3O_2$ dissolves 0.011 gram.

[9] Low recommends disintegration of the fluoride with sulfuric acid, diluting the mixture with water, boiling with ammonium chloride, and then with ammonium hydroxide and hydrogen peroxide. Calcium oxalate is now precipitated from the filtrate and CaO determined by titration with standard permanganate according to the usual procedure for determination of lime.

[10] Compiled by Ernest P. Herner.

[11] Originated by Starck, Z. anorg. allgem. Chem., **70**, 173, 1911. C. A., **5**, 2049, 1911.

[12] Phosphates, sulfates, chromates and arsenates of lead are precipitated, at least in part. Large quantities of alkali salts, boric acid, aluminium and iron prevent complete precipitation of PbFCl. Aluminium causes the greatest trouble. A preliminary acetic acid (1 : 10) extraction will remove most of these radicals. The effect of boric acid and alkali salts is lessened if the solution is allowed to stand longer.

[13] Solubility of PbFCl in 100 grams H_2O: at 18° C. 0.0325 gram, at 100° C. 0.1081.

[14] Best results when .01–.1 gram of fluorine is present.

[15] L. D. Hammond, J. Ind. Eng. Chem., **16**, 938, 1924.

[16] Lundell and Hoffman, J. Research Natl. Bur. Standards, **3**, 581, 1929.

Part 2—One gram NaF dissolved in 100 ml. H_2O, containing 2 ml. of concentrated HCl acid.

The two parts are combined and the precipitate of PbFCl is washed several times by decantation. One liter of cold H_2O is added to the residue and allowed to stand one hour with stirring. The solution is filtered and the clear filtrate used.

Procedure.[17]—One-half gram of the sample dried at 110° C. for one hour is dissolved[18] in about 200 ml. of water and heated to 40° C. The solution is made neutral to methyl-orange indicator and then 3 drops of dilute nitric acid are added. To this solution (or extract from fusion) sixteen drops of concentrated hydrochloric acid are added (possibly 22–24 drops with high grade substance but great excess must be avoided). Ten drops of glacial acetic acid and 25 ml. of the lead acetate solution are added. The heavy white granular precipitate of PbFCl is allowed to stand for one hour, the temperature being kept above 15° C.[19]

The residue is filtered through a weighed Gooch crucible. After washing 3–4 times with the PbFCl solution and finally 1–2 times with cold water the residue is dried one hour at 110°–120° C. and weighed as PbFCl.[20]

Factors: $PbFCl \times 0.16049 = NaF$, or $\times 0.07261 = F$.

Other Methods.—*Precipitation as Triphenyltin Fluoride*[21]

Reagents.—Triphenyltin chloride in 95% alcohol, 0.02 g. per ml.; 95% alcohol saturated with $(C_6H_5)_3SnF$ at room temperature.

Procedure.—The aqueous solution of the fluoride is made up to 60–70% alcoholic by adding the proper volume of 95% alcohol. About twice the calculated quantity of triphenyltin chloride solution, diluted with an equal volume of 95% alcohol is heated to boiling and added slowly into the hot fluoride solution with rapid stirring, and the whole is again heated to boiling and the stirring is continued during part of the cooling. The vessel is allowed to stand overnight since the precipitation is a slow one. The vessel is then cooled in ice for 1 hour, if the amount of fluoride is small. The precipitate is collected on a weighed filtering crucible, washed with the saturated alcoholic wash solution, of which not more than 50 ml. should be required. Dry for 30 minutes at 100–110° C., cool and weigh. Weight of $(C_6H_5)_3SnF \times 0.05153$ = weight of fluorine. The solution should be between pH 7 and 9. The substances which interfere are carbonate, silicic acid and phosphate. Sulfates tend to be precipitated by the alcohol, but moderate amounts of the latter as well as nitrate, chloride, bromide or iodide do not interfere. The method is well adapted for the precise determination of amounts of fluorine ranging from 0.1 to 50 mg. in the absence of the interfering substances that have been mentioned.

[17] Procedure of F. G. Hawley is given above. In the original method of Starck the neutral solution is treated with a large excess of $PbCl_2$ solution. The precipitate is allowed to settle over night, filtered off in a weighed Gooch and washed as directed above. The residue is dried 2–3 hours at 140°–150° C. and weighed as PbFCl.

[18] If the fluoride is not soluble in H_2O it must be fused according to the method of Berzelius and Rose. The H_2O extract of the fusion, after the last trace of silica and ammonia has been removed, is neutralized, made to about 200 ml. and used to precipitate PbFCl.

[19] $PbCl_2$ will crystallize below this temperature.

[20] Because of the limited range and the number of interfering substances it is probably better, when applying this method to complex substances, to precipitate PbFCl as directed, but, instead of weighing, to determine chlorine in the residue according to the volumetric method of Hawley described above.

[21] Allen and Furman, J. Am. Chem. Soc., 54, 4625 (1932).

The general subject of determination of fluorine is considered in the following papers:

In Rocks and in Water, O. Hackl, Z. anal. Chem., **97**, 254 (1934).
Review of Methods, M. Frommes, Z. anal. Chem., **98**, 57 (1934); **99**, 211–223 (1934); **99**, 301 (1934).
In organic compounds, W. Bockemüller, Z. anal. Chem., **91**, 81–90 (1932); J. M. Hubbard and A. L. Henne, J. Am. Chem. Soc. **56**, 1078 (1934).

VOLUMETRIC METHODS FOR THE DETERMINATION OF FLUORINE

VOLUMETRIC DETERMINATION OF FLUORINE[22]

DETERMINATION IN SOLUBLE FLUORIDES

With No Interfering Elements[23] Present.—The reagents used for determining fluorine in solution when no interfering elements are present are as follows:

(1) Zirconium nitrate, 1 g. $Zr(NO_3)_4 \cdot 5H_2O$ in 250 ml. water.
(2) Alizarin red—1 g. of sodium alizarin sulfonate in 100 ml. of ethyl alcohol. Filter off the undissolved residue and add 150 ml. of ethyl alcohol to the filtrate. The two solutions are kept in stock and mixed, 3 parts of solution (1) and two of solution (2) as needed.
(3) Thorium nitrate solution standardized against a known fluoride solution.
(4) Standard fluoride—0.02 N lithium fluoride or specially purified sodium fluoride.
(5) Hydrochloric acid, approximately 1 to 50.

Dissolve a weighed quantity of the fluoride in water and make up to a given volume. Transfer an aliquot of the solution to be analyzed to a small tall-form beaker, add water to make a volume of approximately 20 ml. and 3 drops of the zirconium-alizarin mixture.[24] If necessary, add just enough dilute hydro-

[22] Method of Willard and Winter, Ind. Eng. Chem., Anal. Ed. **5**, 7 (1933).

[23] Any ion which forms a precipitate or a nondissociated salt with fluorine or with thorium interferes with the titration—e.g. Ca^{++}, Ba^{++}, Fe^{+++}, Al^{+++}, PO_4^{---}, etc.

[24] If the volume of the solution to be titrated is sufficiently small (4 to 8 ml.) so that the color can be distinguished, the accuracy of the titration is increased by using only one drop of the indicator. If the volume is large, it may be necessary to add more than 3 drops (50 to 75 ml. require 6 drops). For very accurate results it is necessary to standardize the thorium nitrate in approximately the same volume and with the same number of drops of indicator as the unknown, and titrate the two to the same color. The end point is not sharp in the presence of a large amount of thorium fluoride; not more than 10 ml. of 0.1 N thorium nitrate should be used for the titration.

chloric acid to destroy the color. Add an equal volume of neutral ethyl alcohol, and titrate over a white surface in good light with the standard thorium nitrate to a faint permanent reappearance of color. The reaction is slow near the end point. When titrating with 0.01 N thorium nitrate, make a correction for the fluorine which combines with the indicator. Determine this by titrating the number of drops of indicator used in the titration with 0.01 N fluoride solution to the disappearance of the color.

When interfering elements are present in the soluble fluoride solutions, the fluorine must be separated from the other elements before the titrations can be made. This may be done by volatilizing it as hydrofluosilic acid by simply adding perchloric or sulfuric acid (perchloric acid is preferable since nearly all of the perchlorates are very soluble), water, and several pieces of glass to the sample in a distillation flask, and distilling. When only a small quantity of fluorine (10 mg. or less) is present in the sample and the temperature is not allowed to rise above approximately 125° C., the pieces of glass appear to supply the silica necessary to combine with the fluorine to form hydrofluosilic acid, and there is no noticeable etching of the flask. If there is more fluorine present or the temperature is allowed to rise higher, silica is taken from the flask, and etching is noticeable. In either case, however, the fluorine is recovered quantitatively.

Procedure.—Place the sample in a small distillation flask, and add a few glass beads or pieces of porous plate, 5 ml. of 60% perchloric acid, and sufficient water to cause the solution to boil at 110° C. or less. Place the flask on an asbestos mat with an opening large enough so that about one-third of the flask will be exposed to the flame. Close with a two-hole rubber stopper through which passes a thermometer and a capillary tube, both of which extend down into the liquid. Connect a dropping funnel with the capillary tube so that water may be added during the process of distillation, and fill this with water. Connect the flask with a water condenser. The distillate may be collected in an open container. Distil until the boiling point of the solution reaches 135° C.[25] Titrate with thorium nitrate as previously directed under the determination of soluble fluorides.

When a large amount of silica is present, the following procedure[26] is followed: Fuse 0.5 gram of the sample with 2.5 grams of sodium carbonate, leach the mass with hot water, filter, and wash. Transfer the insoluble residue back to the dish in which it was leached by means of a fine jet with about 50 ml. of hot water, add sodium carbonate to make approximately a 2% solution, boil a few minutes, filter, and wash thoroughly with hot water. To the combined filtrates which should have a volume of 300 ml., add 0.5 gram of zinc oxide dissolved in perchloric acid, boil the alkaline solution for one minute, filter and wash with hot water. Concentrate the filtrate to 200 ml., add a drop of methyl red, neutralize to a very faint pink with dilute perchloric acid, add a solution of 0.25 gram of zinc oxide and 0.5 gram of ammonium carbonate dissolved in 0.5 ml. of ammonium hydroxide and 10 ml. of water. (Place on

[25] Quantitative recovery of fluorine was obtained with the temperature anywhere between 120° C. and 150° C. However, when a large amount of organic material is present, care should be taken to prevent the temperature from rising above 135° C., as otherwise an oxidizing action may occur which is unduly violent. In such cases sulfuric acid may be preferable.

[26] Lundell and Hoffman, J. Research Natl. Bur. Standards, 3, 581 (1929).

steam bath until a clear solution is obtained.) Boil the solution until the odor of ammonia has entirely disappeared, concentrate to about 100 ml., filter, and wash with cold water. Concentrate the filtrate to 25 ml., and either transfer to the distillation flask for the determination of fluorine; or to a 50-ml. volumetric flask, make up to volume, and take an aliquot for the determination.

VOLUMETRIC DETERMINATION OF FLUORINE—FORMATION OF SILICON TETRAFLUORIDE AND ABSORPTION OF THE EVOLVED GAS IN WATER. OFFERMAN'S METHOD[27]

Silicon tetrafluoride is formed by the action of sulfuric acid upon a fluoride in presence of silica, the evolved gas is received in water and the resulting compound titrated with standard potassium hydroxide. The following reactions take place:

A. $3SiF_4+2H_2O=2H_2SiF_6+SiO_2$.

B. $H_2SiF_6+6KOH=6KF+SiO_2+4H_2O$.

The method is suitable for determining fluorine in fluorspar in evaluation of this mineral.

Procedure.—The powdered sample, containing the equivalent of 0.1–0.2 gram calcium fluoride, is mixed with about ten times its weight of pulverized quartz (previously ignited and kept in a desiccator), placed in the decom-

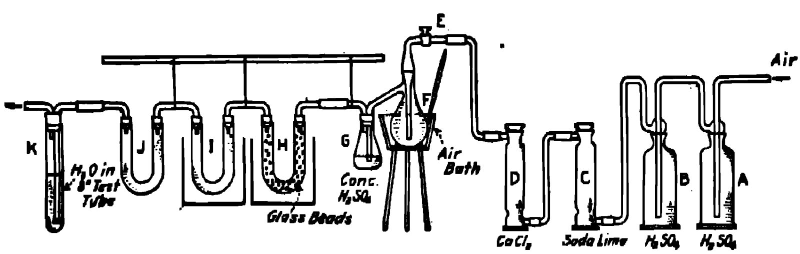


FIG. 50. Adolph's Apparatus for Determining Fluorine.

position flask *F*, shown in Fig. 50, and about 1 gram of anhydrous copper sulfate added, followed by 25 ml. of concentrated sulfuric acid. The stopcock *E* is closed and the air bath heated gradually till in one-half hour the temperature has risen to 220° C. The cock *E* is now opened and air slowly forced through the apparatus (by means of water pump) at the rate of about three bubbles per second, the temperature being kept at 220° C., and the flask containing the sample occasionally shaken. When the bubbles of silicon tetrafluoride have disappeared from *F*, the flame is removed, but the air current continued for half an hour longer. The solution in the receiving flask is now titrated with 0.1 N KOH.

NOTES.—The apparatus shown in the cut is the form recommended by Adolph, and the details of procedure are essentially his. This method is preferred to that of Penfield,[28] in which an alcoholic solution of potassium chloride is used to absorb

[27] Z. angew. Chem., 3, 615, 1890. Wm. H. Adolph, J. Am. Chem. Soc., 37, 11, 2500, 1915.

[28] Am. Chem. Jour., 1, 27, 1879.

the tetrafluoride, and the liberated hydrochloric acid titrated with the standard alkali in presence of cochineal indicator.

The results obtained by this method are generally low, but the procedure is useful for rapid valuation of fluorspar.

The run having been made as directed, the solution in tube K is poured into a beaker, an excess of standard potassium hydroxide added and the excess alkali titrated with standard sulfuric acid in boiling solution. Norris prefers the use of litmus indicator to phenolphthalein, claiming that the end-point is sharper.

It is found advisable to use mercury in the tube K as a trap, thus preventing the stoppage of the delivery tube by crystallization. The gas readily passes up through the mercury and is absorbed in the supernatant solution.

In place of using N/10 solutions the potassium hydroxide may be made of such strength that 1 ml. will equal 1% fluorine with 0.5 g. sample taken and the acid made to a corresponding strength.

NOTES.—The following suggestions for the method are made by W. V. Norris, Colorado School of Mines.

It is especially necessary that all apparatus be dry, as the least amount of moisture will make the results run low. For this reason it is better to use phosphoric anhydride in washing bottle B instead of sulfuric acid.

The sulfuric acid used should be previously treated as follows: Heat 500 ml. of acid to white fumes, cool, warm gently but not to fumes, then again cool in a desiccator until ready for use. This will produce an acid that will be an efficient dehydrator and will give off no free sulfur trioxide.

It is advisable to use a large excess of silica in the generator apparatus, preferably ten times the weight of the sample taken.

The copper sulfate must be anhydrous, and can best be obtained by heating very thin layers of the pure blue crystals in an oven for about five hours at 215° C.

Adhere strictly to the directions of keeping the temperature in the flask at 220° C., as that temperature will give the maximum recovery.

The bottles A, B, C and D are for the purpose of thoroughly drying the air. G contains conc. sulfuric acid, prepared as suggested above. H is filled with glass beads, to remove sulfuric acid spray; I and J are empty tubes which should be thoroughly dry. The gas is completely absorbed in tube K.

COLORIMETRIC DETERMINATION OF FLUORINE—METHOD OF STEIGER[29] AND MERWIN[30]

The method is based on the bleaching action of fluorine upon the yellow color produced by oxidizing a solution of titanium with hydrogen peroxide. A known amount of titanium in solution is mixed with definite volume of the solution containing the fluorine and the tint compared with a standard solution containing an equivalent amount of titanium. The extent of bleaching enables the computation of the fluorine present. The method is applicable to determination of fluorine in amounts ranging from 0.00005 to 0.01 gram. Merwin has shown that large amounts of alkali sulfates have a bleaching action similar to fluorine. Addition of free acid, or rise of temperature, intensifies the color lost by bleaching. Aluminum sulfate has no marked effect on standard solutions, or on solutions bleached by alkali sulfates, but it restores the color

[29] G. Steiger, J. Am. Chem. Soc., 30, 219, 1908.

[30] H. E. Merwin, Am. Jour. Sci. (4), 28, 119, 1909. C. A., 3, 2919, 1909. J. W. Mellor, "A Treatise on Quantitative Inorganic Analysis." Chas. Griffin & Co.

to a considerable degree to solutions bleached by fluorine. Ferric sulfate has a similar effect. Phosphoric acid bleaches a standard solution. Silica has little effect. According to Merwin an accuracy of 0.002 gram may be expected, an error which is half that of the most reliable gravimetric method.

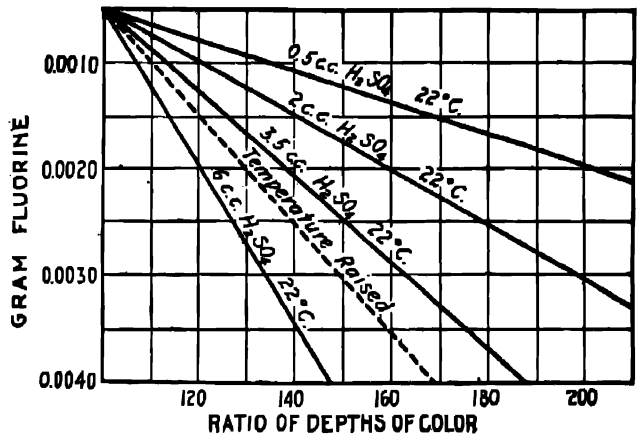


FIG. 51. Effect of Sulfuric Acid upon the Color.

Reagents. *Standard Titanium Solution.*—An intimate mixture of 1 gram of TiO_2 and 3 grams of ammonium persulfate is heated until the vigorous action has ceased, and the ammonium sulfate is expelled. The residue is treated with 20 ml. of conc. sulfuric acid, heated to fuming and, when cold, poured into about 800 ml. of cold water. When the suspended salt has dissolved, 57.5 ml. of conc. sulfuric acid are added, and the solution made up to 1000 ml. (50 ml. or more of the solution should be analyzed for TiO_2). *One ml. will contain* 0.001 *gram* TiO_2.

Standard Fluorine Solution.—2.21 grams of sodium fluoride, which has been purified by recrystallizing, washing, and igniting strongly, is dissolved in 1000 ml. of water. One ml. will contain 0.001 gram fluorine.

Sulfuric Acid.—95.5% solution, (sp.gr. 1.84).

Hydrogen Peroxide.—Ordinary strength.

Standard Colored Solution.—The solution used in determining fluorine in materials fused with alkali carbonates contains 10 ml. of the titanium solution, 4 ml. of hydrogen peroxide, and 4 ml. of concentrated sulfuric acid.

Apparatus.—*Nessler Tubes* 6 cm. long, 2.7 cm. in diameter are recommended by the authors. Colorimeters may be used in place of Nessler tubes. A very suitable type for this purpose is shown on page 292, Fig. 38.

Procedure.—Two grams of the powdered sample are fused with 8 grams of mixed sodium and potassium carbonates, the fusion taken up with hot water, and, when leached, 3 to 4 grams of ammonium carbonate added. The mix is warmed for a few minutes and then heated on the water bath till the ammonium carbonate is decomposed and the bulk of liquid is small. Silica, ferric oxide, and alumina oxide are thrown down and are removed by filtration. The filtrate, which should not exceed 75 ml., is treated with 4 ml. of hydrogen peroxide, and then 10 ml. of standard titanium solution cautiously added (H_2O_2 prevents

precipitation of TiO_2 by the alkali carbonates), followed by 4 ml. of conc. sulfuric acid to neutralize the alkali carbonates. The solution, neutral or slightly acid, acquires a light orange tint. A little sodium carbonate is added in just sufficient amount to discharge the color, and then a drop or so of acid to again restore it. The amount of excess acid now required depends upon the amount of fluorine present in the solution. For amounts of fluorine less than 0.0025 gram (0.125% of sample), 3 ml. of acid are added. For amounts of 0.0025 to 0.012 gram fluorine, 12 ml. of acid are added. The solution is diluted to 100 ml.

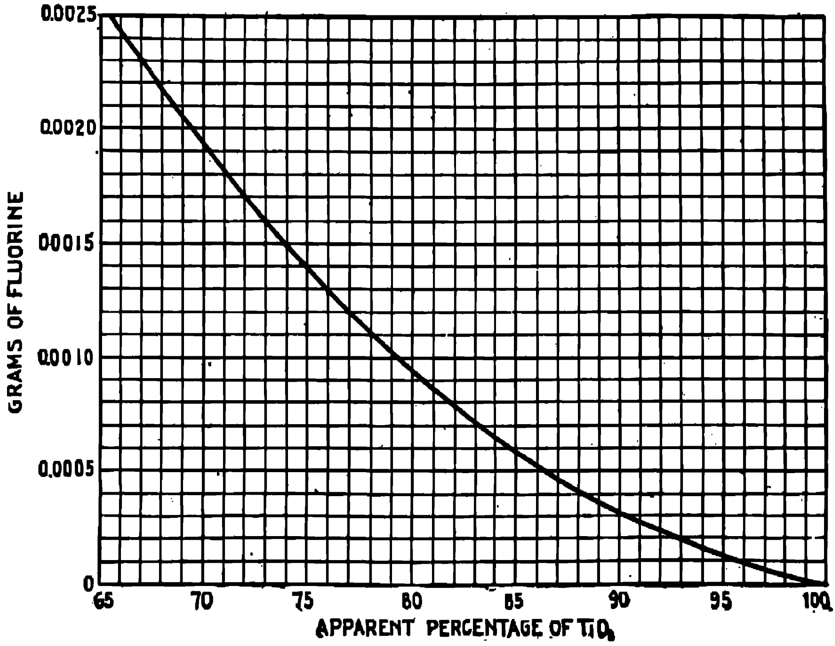


FIG. 52. Fluorine—Titanium Ratio.

Comparison.—The test solution is now compared with the standard solution containing 10 ml. titanium reagent, and the same amount of acid and hydrogen peroxide as in the test sample, in a volume of 100 ml. If Nessler tubes are used, these are held over a white surface illuminated with diffused light. In the absence of a bleaching substance, such as fluorine, the two solutions will have the same tint, but in presence of fluorine the bleaching effect will cause the test solution to appear paler than the standard. The depths of the liquids are adjusted so that the tubes will have the same intensity of color when moved from right to left or reversed. Should the left eye perceive a darker shade, the tube on the left will appear uniformly darker whether it be the test sample or the standard. The comparative depths of the liquids in the tubes are measured and the ratio obtained by dividing the depth of the fluorine solution by the depth of the standard and multiplying by 100. Reference may be made to the plotted curve shown in Fig. 52. The ratio $\frac{\text{Depth of F Sol.}}{\text{Depth of Standard}} \times 100 =$ the

abscissa, while the ordinate represents the amount of fluorine in the 2-gram sample.

Example.—Suppose the test solution = 3.6 ml. and the standard = 4.5 ml.; the ratio then = 80; from the curve it is evident that the fluorine = 0.00095 gram or 0.0475%, since a 2-gram sample was taken.

NOTES.—1. The destruction of ammonium carbonate is necessary because ammonium sulfate bleaches the final solution and should be absent.

2. Changes of temperature of 50° C. intensify the color 5 to 15%.

3. Increasing the acidity tends to restore the bleached color.

4. The same ratios are obtained by dividing the final volume of the standard by the volume of the test in cases in which a colorimeter is used which requires the standard to be diluted.

According to Merwin, however, the bleaching effect of alkali sulfates, which are present, will make the ratio much higher than it would be if they were absent. (The sulfates alone give a ratio of 125.) This ratio should be determined on two 8-gram portions of the alkali carbonate mixture used in the fusion and the correction made accordingly. If this ratio, represented by m and r, is the ratio of the two solutions, then $(r-m) \div 23{,}000 =$ g. F for amounts of fluorine not exceeding .0025 g. (3 ml. H_2SO_4, 22° C.; 4 ml. H_2O_2, .01 g. TiO_2). If the fluorine amounts to .0025 to .012 g., then 12 ml. H_2SO_4 is added and the formula required is $(r-m-3) \div 6300 =$ g. F (m blank should be determined and should not much exceed 108). In absence of sulfates the following formulas are given—

(a) $(r-100) \div 70{,}000 =$ g. F, with .5 ml. H_2SO_4, limits of F = .00005 to .001 g.
(b) $(r-100) \div 22{,}000 =$ g. F, with 3.5 ml. H_2SO_4, limits of F = .001 to .004 g.

Example (a) if $r = 142$, then $(142-100) \div 70{,}000 = .0006$ g. F.

See also "Determination of Fluorine"—an indirect method recommended by F. G. Hawley, J. Ind. Eng. Chem., 18, 572, 1926.

THE VOLUMETRIC DETERMINATION OF FLUORINE [31]

Two procedures are suggested—a rapid method depending upon the estimation of fluorine from the percentage of calcium present with fluorine, the calcium combined with commonly occurring substances being extracted by glacial acetic acid; and a procedure that depends upon separation of fluorine from its combination by converting it to soluble alkali salt and reprecipitating it from solution by addition of a known amount of calcium salt, the excess of the calcium being converted to oxalate and so determined, the amount combined with fluorine being thus estimated and the equivalent fluorine calculated.

REAGENTS

Calcium Acetate (0.25 N solution).—12.51 grams of pure calcium carbonate are dissolved in 500 ml. of water and 75 ml. glacial acetic acid (large beaker

[31] By Wilfred W. Scott. Reprinted from J. Ind. Eng. Chem., 16, 703 (1924).

necessary) and the acetate formed is placed in a graduated flask and diluted to 1000 ml. The solution is standardized by precipitation of the calcium oxalate in an aliquot portion (40 ml.) and titration with standard potassium permanganate. Exact normality is recorded.

1 ml. 0.25 N solution = 0.005 gram calcium.

Potassium Permanganate (0.25 N solution).—7.91 grams of pure crystals ($KMnO_4$) per liter are standardized against 0.67 gram of pure sodium oxalate equivalent to 40 ml. 0.25 N solution. Exact normality is recorded.

Sodium Oxalate (0.25 N solution containing 16.75 grams of the salt per liter).—Solution is best effected in hot water. (Solubility, 3.22 grams per 100 ml. at 15° C.)

PRELIMINARY PROCEDURE

(a) **Minerals Containing Phosphates or Sulfates.**—One gram of the finely powdered mineral, ore, or calcium fluoride salt is extracted with 50 ml. of dilute acetic acid (1 part glacial, 10 parts water) by gently warming for 15 to 20 minutes with stirring. The residue, transferred to a small, ashless filter, is washed with about 50 ml. of water, making the total extract 100 ml. (Save for calcium determination, if desired.) The filter and residue are dried rapidly by spreading out on a watch glass. The fluoride is carefully transferred onto a sheet of glazed paper, the filter ignited, and the ash added to the fluoride. The residue is fused as directed under Fusion.

NOTE.—For exact work an allowance has to be made for the solubility of the calcium fluoride. The following solubilities were found, 0.5-gram samples of material being taken and treated with 100 ml. of acetic acid of the strength stated:

Acid	H_2O	CaF_2	$CaCO_3$	Ca_3PO_4	$CaSO_4$
1 part	2 parts	0.0103	Very soluble	0.240	0.084
1 part	10 parts	0.0144	Very soluble	0.276	0.170

(b) **Phosphates and Sulfates Absent.**—No acetic acid extraction is necessary.

(c) **Sulfides Present.**—Sulfur as sulfide occurs generally combined with iron, copper, cobalt, etc. No special procedure is necessary here, as the sulfide is oxidized later.

Fusion.—Five grams of sodium carbonate and 10 grams of potassium hydroxide, placed in a 50- to 60-ml. silver or iron crucible, are brought to quiet fusion, and allowed to cool until a crust forms over the melt. Half a gram of the fluoride sample is intimately mixed with 0.5 to 1 gram of powdered silica prepared as outlined above (powdered sand free of fluorine will do), and placed in the crucible over the fusion. The crucible is covered and heat applied to bring the contents of the crucible to molten temperature. (High heat is not necessary.) Complete decomposition is effected in half to three-quarters of an hour. The crucible should be agitated frequently during fusion to mix the contents.

NOTE.—Calcium fluoride is not so easily decomposed as many existing methods indicate. Hydrochloric acid apparently dissolves the mineral, but on dilution calcium fluoride precipitates. Sulfuric acid and potassium acid sulfate fusion is far from satis-

factory; platinum is required and a loss due to bumping is liable to occur. Complete decomposition by acid treatment is frequently doubtful. The alkali fusion appears to be the best method for decomposing the fluoride.

If the mass is in molten condition, it may be poured in the lid of the crucible; if too viscous to pour, it is spread over the inner surface of the crucible by rotating the crucible over the flame. The material is now disintegrated and removed from the crucible and lid by action of about 200 ml. of hot water in a 500-ml. beaker. Ten milliliters of hydrogen peroxide are added and the solution is boiled for about 5 minutes.

NOTE.—Fusions made in silver disintegrate more readily than those made in iron. Calcium carbonate tends to adhere to the walls of the crucible.

Boiling the solution expels the excess of peroxide, which interferes in the oxalate precipitation of calcium, if left in solution. Sulfides, iron, and other oxidizable materials are oxidized by the peroxide.

The solution containing the excess of sodium carbonate, potassium hydroxide, alkali fluoride, and the greater portion of the silica is filtered off; the residue, containing calcium carbonate (or phosphate if present in the fused material), silver, iron, some silica (10 to 15% of total), etc., is washed with hot water (10 times) and the washings are combined with the first filtrate. The residue is used for Procedure A, the filtrate for Procedure B.

NOTE.—Should phosphates be present in the material, the greater portion will remain in the residue, and a small amount will pass into the filtrate as sodium salt.

$$Ca_3(PO_4)_2+3Na_2CO_3 \rightleftharpoons 3CaCO_3+2Na_3PO_4.$$

PROCEDURE A—DETERMINATION OF CALCIUM AND EQUIVALENT FLUORINE

The residue washed into a beaker is dissolved in hydrochloric acid (200 ml. of water, 20 ml. HCl). If any gritty material remains, it is advisable to fuse this with about 2 grams of sodium carbonate and 3 to 5 grams of potassium hydroxide, repeating the extraction with water; the residue is dissolved in hydrochloric acid and added to A and the water extract to B. The free acid is neutralized with ammonia, the solution heated and filtered, and the residue washed. Calcium passes into solution, iron (and silver) remains on the filter. (The crucible should be rinsed out with dilute hydrochloric acid, as calcium carbonate may adhere to the walls of the vessel.)

NOTE.—A small amount of calcium is liable to be occluded by the hydroxide of iron. If this is present in appreciable amount, it is necessary to dissolve this in hydrochloric acid, reprecipitate with ammonia, and filter, adding the filtrate to the main portion containing calcium.

Calcium is now precipitated from the filtrate by adding 0.25 N sodium oxalate. About 60 ml. are necessary for 0.5 gram of calcium fluoride (fluorspar). After heating to crystallize the oxalate, the calcium is filtered off, washed with water (6 times), dissolved in water containing sulfuric acid (200 ml. H_2O+10 ml. H_2SO_4), and titrated hot with 0.25 N potassium permanganate.

$$1 \text{ ml. } 0.25 \text{ N } KMnO_4 = 0.005 \text{ gram Ca and } 0.00474 \text{ gram F.}$$

Note.—If the mineral was extracted with dilute acetic acid (1 : 10) to remove calcium phosphate, carbonate, or sulfate, an allowance should be made for the solubility of calcium fluoride of approximately 0.014 gram CaF_2 per 100 ml. extract at 18° C.

If total calcium is desired, the calcium in the extract should be determined and added to the calcium of the fluoride.

PROCEDURE B—DETERMINATION OF FLUORINE. CALCIUM ACETATE METHOD

The alkaline filtrate (water extract of the fusion) contains the fluorine, sodium and potassium salts, and silicic acid.

The filtrate is heated to near boiling and sufficient 0.25 N calcium acetate reagent is added to precipitate all the fluorine and about 5 to 10 ml. excess (60 ml. per 0.5 gram CaF_2). Glacial acetic acid is now added until faintly acid (if the solution is alkaline, litmus paper test) and then an excess of 1 ml. per 100 ml. of solution. The heating is continued for about 5 minutes.

Note.—Upon addition of the calcium acetate, calcium carbonate also precipitates with calcium fluoride. When the solution becomes acid, the carbonate dissolves. If the acidity is correct, the precipitate settles readily and is easily filtered. Should it be finely divided and remain in suspension, the addition of sufficient potassium or sodium hydroxide to give an alkaline reaction will coagulate and settle the precipitate.

The solution and precipitate are transferred to a 500-ml. (or larger) graduated volumetric flask and, after cooling (18° C.), made to volume, then transferred to a large beaker and the precipitate allowed to settle for a few minutes. An aliquot portion of the clear solution is decanted through a filter, the first 5 to 10 ml. being rejected (several filters may be used to hasten filtration, if slow). A measured volume of the filtrate is now taken for the determination of excess calcium.

Precipitation and Titration of Calcium.—Sufficient 0.25 N sodium oxalate solution is added to precipitate the calcium. It is safe to use as much oxalate as the aliquot requires in case no calcium was removed by fluorine—i.e., if one-half the total solution represents the aliquot, then 30 ml. of oxalate are added. The author prefers to precipitate the calcium from a weak acetic acid solution (about 0.5 ml. free glacial acetic acid per 100 ml.). This is the acidity of the solution obtained on adding calcium acetate and acetic acid, as directed, no alkali being added, as suggested, for settling stubborn calcium fluoride precipitates.

The calcium oxalate is coagulated by heating, then filtered, washed, and titrated with 0.25 N potassium permanganate in a hot solution containing sulfuric acid. The oxalate is best dissolved from the filter by hot water containing sulfuric acid.

1 ml. 0.25 N potassium permanganate = 0.005 gram calcium.

Calculation.—If A = ml. 0.25 N calcium acetate,

B = ml. 0.25 N potassium permanganate,

X = factor for converting the aliquot portion of solution taken in the calcium determination to total solution.

Then A ml. $-XB$ ml. = ml. 0.25 N calcium acetate required by fluorine. The difference multiplied by 0.005 = calcium combined with fluorine, or multiplied by 0.006 = equivalent fluorine ($Ca \times 1.2 = F$). (See Discussion.)

CORRECTION.—Owing to the slight solubility of calcium fluoride and possibly to the formation of a complex compound, calcium fluoride with a fluosilicate, a corrective factor seems to be necessary, the ratio of calcium to fluorine being 40 : 48, rather than the ratio represented in the formula CaF_2.

PROCEDURE C—DETERMINATION IN ALKALI FLUORIDES

Decomposition.—0.5 to 1 gram of the alkali fluoride is dissolved in about 100 ml. of hot water.

Precipitation.—The fluorine is precipitated by adding, from a burette, a known amount of 0.25 N calcium acetate in sufficient amount to precipitate all the fluorine, and then 5 to 10 ml. in excess. If the solution has not become acid by addition of the reagent, make it so by adding acetic acid. The solution and precipitate are transferred to a 250-ml. graduated flask, and after cooling are made to volume and well mixed. An aliquot portion is now filtered through a fine-mesh filter (rejecting the first 5 to 6 ml.). A measured portion (half the original total is recommended) is heated to boiling, and calcium is precipitated by adding an excess of sodium oxalate. The solution is neutralized with ammonia and the calcium oxalate filtered off, washed, and titrated with 0.25 N potassium permanganate, according to the standard procedure. (See Precipitation and Titration of Calcium.)

Calculations of Fluorine.

If A = total ml. of 0.25 N calcium acetate,

B = ml. of 0.25 N potassium permanganate required by the calcium in half the total volume.

Then $A-2B = \%$ fluorine per half gram sample or $(A-2B) \times 0.005 \times 0.948$ = gram fluorine.

NOTES.—It appears that the compound formed by addition of calcium acetate to the soluble fluoride is CaF_2; it is thus possible to use the conversion factor 0.948 for converting the calcium, combined with fluorine, to its equivalent fluoride.

The method does not distinguish fluorine combined as a fluosilicate from fluorine combined as a fluoride.

The best method for decomposing fluorspar or calcium fluoride was found to be by fusion with sodium and potassium carbonates, sodium carbonate and potassium hydroxide, or sodium or potassium carbonate and sodium hydroxide. The presence of silica is necessary.

CaF_2 is precipitated by adding the calcium acetate reagent to the alkaline solution of the fluoride. The calcium carbonate, which also forms, redissolves as soon as the solution becomes acid. A large amount of acid is to be avoided, as this liberates silicic acid, which prevents the settling of the fluoride. When the solution is first acidified and the calcium fluoride is then precipitated, the compound settles badly and is difficult to filter. Should the fluoride be difficult to settle, it is preferable to make the solution alkaline by addition of sodium or potassium hydroxide, rather than to add an insoluble substance to carry down the flocculent material. The alkali treatment coagulates the fluoride (probably dissolving silicic acid) and causes rapid settling.

VOLUMETRIC DETERMINATION OF FLUORINE[32]

The Method of Hawley.—Fluorine is precipitated as PbFCl, using hydrochloric acid and lead acetate. The chlorine contained is determined by some standard method for chlorine and fluorine is calculated from the results. This procedure is applicable in the presence of fairly large amounts of the radicals that interfere in the gravimetric procedure. It can be used nearly equally as well with simple fluorides as with complexes such as topaz, mica, insecticides and other artificial mixtures. The method is especially well adapted to ores and mineral substances. Insoluble substances must be rendered soluble by fusion. The accuracy on low-grade materials is somewhat better than that of the Berzelius CaF_2 method.

Reagents.—*Lead acetate:* 10% lead acetate solution containing 1% glacial acetic acid.

Wash solution: Saturated PbFCl solution for washing. (For preparation see gravimetric method, page 405.)

Procedure.—Preparation of material: One-half gram of the dried sample is fused[33] with 7–8 grams of sodium-potassium carbonate mixture (1 : 1) in a platinum[34] crucible. About 4 times as much silica as fluorine should be present (a great excess should be avoided). Sulfur, if present, should be oxidized here with H_2O_2 or Na_2O_2 (an excess should be avoided; this treatment lowers the accuracy).

When well fused the mass is placed on a smooth metal plate and allowed to cool. The dish[34] and melt are heated with water in a casserole until completely disintegrated and then filtered. Any lumps remaining are heated with 1 gram of Na_2CO_3[35] and thoroughly washed with hot H_2O. The washings are added to the above filtrate.

The beaker containing the filtrate (150–250 ml.) is covered and 16 drops of concentrated HCl are added (high grade substance may require 22–24 drops but much more will precipitate $PbCl_2$).[36]

The solution is warmed to 40° C. and enough HNO_3 is added to make neutral to methyl-orange and to leave 3 drops in excess.

Precipitation of PbFCl.—Ten drops of glacial acetic acid and 25 ml. of the clear lead acetate are added. The precipitate of PbFCl, dense and granular, forms usually at once but the precipitation may not be complete for 30–60 minutes. The solution is stirred and cooled. The temperature must not fall below 15° C. or $PbCl_2$[36] will crystallize; other Pb salts may precipitate here but they will not make a great deal of difference. The precipitate is filtered off (on fine paper), washed, first with a small amount of cold H_2O,[37] then with PbFCl 3–4 times and finally 1–2 with cold H_2O.

[32] Compiled by Ernest P. Herner.

[33] If the fluoride is soluble the fusion may be omitted, but this seldom is the case in ores.

[34] A porcelain crucible may be used; if so it should be broken and boiled with the melt in extracting.

[35] The second boiling usually recovers all the fluorine, but with high fluorine content refusion increases the accuracy.

[36] $PbCl_2$ crystals can be recognized by their needle-like structure, transparency and high luster. They are also more soluble in H_2O than PbFCl.

[37] Accuracy is much decreased if pure water is used for washing.

Determination of Chlorine.—Dissolve the PbFCl precipitate by pouring 20–30 ml. of hot 25% nitric acid through the filter. The mixture should be heated on a steam bath.[38]

The chlorine can now be determined by any standard method. The silver nitrate method of Volhard may be used, the silver may be deposited by electrolysis or silver chloride may be cupelled.

VALUATION OF FLUORSPAR

The following procedure, worked out by Dr. Bidtel,[39] meets the commercial requirements for the valuation of fluorspar. The determinations usually required are calcium fluoride, silica, and calcium carbonate; in some particular cases lead, iron, zinc, and sulfur.

Procedure. Calcium Carbonate.—One gram of the finely powdered sample is placed in a small Erlenmeyer flask, 10 ml. of 10% acetic acid are added, a short-stemmed funnel inserted in the neck of the flask as a splash trap, and the mixture heated for an hour on a water bath, agitating from time to time. The calcium carbonate is decomposed and may be dissolved out as the soluble acetate, whereas the fluoride and silica are practically unaffected. The solution is filtered through a 7-cm. ashless filter, the residue washed with warm water four times, and the filter burned off in a weighed platinum crucible at as low a temperature as possible. The loss of weight minus 0.0015 gram (the amount of calcium fluoride soluble in acetic acid under the conditions named) is reported as *calcium carbonate.*

Silica.—The residue in the platinum crucible is mixed with about 1 gram of yellow mercuric oxide, in form of emulsion in water (to oxidize any sulfide that may be present); any hard lumps that may have formed are broken up, the mixture evaporated to dryness and heated to dull redness, then cooled and weighed. About 2 ml. of hydrofluoric acid are added and the mixture evaporated to dryness. This is repeated twice to ensure complete expulsion of silica (as SiF_4). A few drops of hydrofluoric acid are then added, together with some macerated filter paper, and a few drops of ammonium hydroxide to precipitate the iron. The solution is evaporated to dryness, heated to dull redness, cooled and weighed. The loss of weight is reported as *silica.*

[38] Much heat must not be used for there is danger of dispelling some chlorine. If there is a great deal of PbFCl it may not dissolve readily, but this does not matter unless much $PbSO_4$ is present. This will interfere later if not removed here; but since PbFCl is very soluble in nitric acid and $PbSO_4$ is not, a separation can be effected by filtering.

[39] E. Bidtel, J. Ind. Eng. Chem., 4, 201 (1912).

Calcium Fluoride.—The residue is treated with 2 ml. of hydrofluoric acid and 10 drops of nitric acid (to decompose the oxides), the crucible covered and placed on a moderately warm water bath for thirty minutes, the lid then removed and the sample taken to dryness. The evaporation with hydrofluoric acid is repeated to ensure the transposition of the nitrates to fluorides, and if the residue is still colored, hydrofluoric acid again added and the mixture taken to dryness a third time; then a few drops of hydrofluoric acid are added and 10 ml. of ammonium acetate solution (the acetate solution is made by neutralizing 400 ml. of 80% acetic acid with conc. ammonia, adding 20 grams of citric acid and making the mixture up to 1000 ml. with conc. ammonium hydroxide). The mixture is digested for thirty minutes on a boiling water bath, then filtered and washed with hot water containing a small amount of ammonium acetate, and finally with pure hot water. (Several washings by decantation are advisable.) The residue is ignited in the same crucible and weighed as *calcium fluoride*. An addition of 0.0022 gram should be made to compensate for loss of CaF_2.

Pure calcium fluoride is white. To test the purity of the residue, 2 ml. of sulfuric acid are added and the material taken to fumes to decompose the fluoride; 1 ml. of additional sulfuric acid is added and the excess of acid expelled by heating. The residue is weighed as calcium sulfate. This is now fused with sodium carbonate, and the fusion treated with hydrochloric acid in excess. If barium is present the solution will be cloudy ($BaSO_4$).

ANALYSIS OF SODIUM FLUORIDE

Preparation of the Sample and Insoluble Residue.—Ten grams of the sample are dissolved in 250 ml. of water in a beaker, and boiled for five minutes, then filtered into a liter flask through an ashless filter; the residue is washed with several portions of water and ignited. This is weighed as insoluble residue. The filtrate and washings are made to 1000 ml. with distilled water.

Sodium Fluoride.—Fifty ml. of the solution equivalent to 0.5 gram of sample are diluted to 200 ml. in a beaker, 0.5 gram sodium carbonate is added and the mixture boiled. An excess of calcium chloride solution is now added slowly and boiled for about five minutes. A small amount of paper pulp is added to prevent the precipitate from running through the filter, the precipitate allowed to settle and then filtered, using a 9-cm. S. & S. 590, or B. & A. grade A, filter paper. The fluoride is washed twice by decantation, and four or five times on the filter with small portions of hot water. The final washings should be practically free of chlorine.

The residue is ignited in a platinum dish, then treated with 25 ml. of acetic acid, and taken to dryness. This treatment is repeated and the residue taken up with a little hot water and filtered. The calcium fluoride is washed free of calcium acetate with small portions of water, remembering that CaF_2 is slightly soluble in water. The ignited residue is weighed as CaF_2.

$$CaF_2 \times 1.0758 = NaF.$$

Sodium Sulfate.—To the filtrate from calcium fluoride is added 10 ml. hydrochloric acid and then a hot solution of barium chloride. The $BaSO_4$ is allowed to settle, filtered, washed, dried, ignited, and weighed as usual.

$$BaSO_4 \times 0.6086 = Na_2SO_4.$$

Sodium Carbonate.—Sodium carbonate is determined on a 5-gram sample by the usual method for carbon dioxide as described in the chapter on Carbon.

Approximate results may be obtained by adding a small excess of normal sulfuric acid to 5 grams of the fluoride in a platinum dish, boiling off the carbon dioxide, and titrating the excess of acid with normal caustic, using phenolphthalein indicator.

$$\text{One ml. N } H_2SO_4 = 0.053 \text{ gram } Na_2CO_3.$$

$$H_2SO_4 \times 1.0808 = Na_2CO_3.$$

Sodium Chloride.—Fifty ml. of the sample is titrated with N/10 $AgNO_3$ solution.

Silica.—This is probably present as sodium silicofluoride and silicate. One gram of the sample is dissolved in the least amount of water and a small excess of hydrofluoric acid added to convert the silicate to silicofluoride, then an equal volume of alcohol. After allowing to stand for an hour, the precipitate is filtered, washed with 50% alcohol until free of acid and the filter and fluoride are placed in a beaker with 100 ml. of water, boiled and titrated with N/10 NaOH.

$$\text{One ml. N/10NaOH} = 0.0015 \text{ gram } SiO_2 \text{ or } 0.0047 \text{ gram } Na_2SiF_6.$$

Volatile Matter and Moisture.—One-gram sample is heated to dull redness to constant weight. Loss of weight is due to moisture and volatile products.

DETERMINATION OF TRACES OF FLUORINE

An approximate estimation of traces of fluorine may be made by utilizing the method outlined for detection of this element. By varying the amounts of substance tested, an etch is obtained that is comparable with one of a set of standard etches, obtained with known amounts of fluorine in form of calcium fluoride, added to the same class of material examined.

The conditions in obtaining the standard etches and those of the tests should be the same. This applies to the temperature of the paraffine bath, duration of the run, size of mark exposing the surface of the test-plate, and the general mode of procedure.

One gram of sample is placed in a lead bomb with 12 ml. of sulfuric acid, the bomb closed with glass plate in place and heated in an oil bath for 45 minutes at 165° C. The etching on the glass plate is compared with etching using known amounts of fluorine as CaF_2 and the same kind of glass.

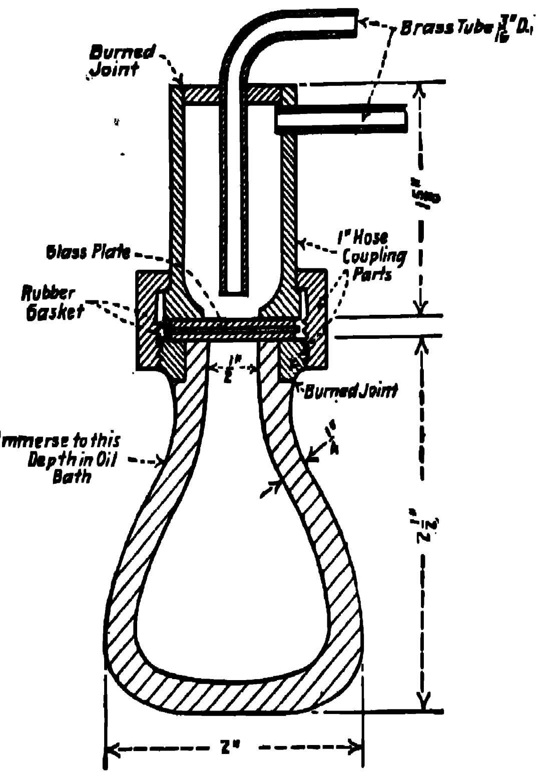


FIG. 53. Apparatus for Determining Traces of Fluorine

The glass plate is kept cool by circulating cold water. The type of bomb and its connections are shown in Figure 53.

NOTE.—The importance of regulating the temperature may be seen by the results obtained by Woodman and Talbot. With a temperature of 79–80° C., one part of fluorine may be detected in 25 to 100 thousand parts of material; by raising the temperature to 136° C., the delicacy of the procedure is increased to one part of fluorine in 1 to 5 million parts. The limit of delicacy is apparently reached at 213–218° C. (i.e., 1 part F per 25 million).

A metal condenser, such as is recommended for mercury determinations, may be used and the oil or paraffin bath substituted for an electric heater automatically controlled.

Crisco is claimed to be better than paraffin, as this does not give off any unpleasant fumes when heated.

DETECTION AND ESTIMATION OF SMALL AMOUNTS OF FLUORINE [40]

Zirconium Purpurin Test

Reagent.—The following substances are necessary to make one liter of the reagent: *0.16 gram of zirconium oxychloride, 9 mg. of purpurin (1, 2, 4-trihydroxyanthraquinone), 30 ml. of ethanol, and 720 ml. of concentrated hydrochloric acid.*

The zirconium salt is dissolved in 100 ml. of concentrated hydrochloric acid, 100 ml. of water being added to insure a clear solution. The purpurin is dissolved in the alcohol and the resulting solution added slowly with continuous shaking to the zirconium solution. The remainder of the hydrochloric acid is then added and the solution made up to 1 liter with water. It is essential that the purpurin be added to the zirconium solution and not vice versa, since otherwise the solution becomes cloudy. The mixture is allowed to stand overnight and is then ready for use. The reagent is stable for at least 1 month. After 2 or 3 months the color begins to fade and a precipitate forms.

In the absence of interfering substances, the solid, or residue obtained after evaporating the solvent, is dissolved in 2 ml. of 6 N hydrochloric acid and 2 ml. of the reagent are added. The pink color of the reagent will turn yellow immediately if 0.003 mg. or more of fluoride is present. To confirm the presence of fluorine, solid zirconium oxychloride is added a little at a time with shaking. The color should turn pink again. If it does not, or if a cloudy or orange solution results after the addition of the purpurin-zirconium reagent, the presence of interfering elements which have destroyed the dye is indicated. The final acidity of the mixture should be between 7 N and 10 N with respect to hydrochloric acid. If the acidity is greater than 10 N, the color in the absence of fluorine is orange or yellow; if less than 6 N, a cloudy solution forms. The test becomes impossible at acidities of less than 4 N.

Distillation Method.—The fluoride is distilled off as silicon tetrafluoride, which is collected in the pink purpurin-zirconium reagent. The distillation apparatus consists of a wide-mouth Pyrex flask of about 150 ml. capacity. It is fitted with a ground-glass stopper containing an inlet tube extending to the bottom and a second tube ending below the neck of the flask, the other end of which is bent down and sealed in a small test tube.

The dry sample is introduced into the flask with about 1 gram of quartz or silica powder and 25 ml. of concentrated sulfuric acid. One milliliter of the purpurin-zirconium reagent is put into the small test tube. A stream of air, dried by concentrated sulfuric acid, is passed through the flask and the latter heated to 140° C. in an oil bath. It is essential that the entire apparatus be perfectly dry before the test is begun. The temperature should never exceed 160° C. A blank test run for 1 hour without any fluoride gives no change in color of the reagent in the small test tube. Longer heating results in a gradual change of color of the reagent to orange. The speed with which the reagent changes color depends on the amount of fluoride present.

[40] I. M. Kolthoff and Maurice E. Stansby, Ind. and Eng. Chem., Anal. Ed., 6, 118 (1934).

Quantitative Estimation

Reagents Required.—300 mg. of purpurin in a liter of ethanol; and 10 N hydrochloric acid; zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) in 10 N hydrochloric acid, containing 0.8 gram of zirconium per liter; and a solution of 19.60 grams of cobalt nitrate [$CO(NO_3)_2 \cdot 6H_2O$] and 0.132 gram of potassium dichromate per liter of water, kept in a glass-stoppered bottle.

Procedure.—For the determination of 0.5 to 15 mg. of fluoride the fluoride sample is introduced into an oil-sample bottle of 100 ml. capacity. If it is a solid, 2 ml. of water should be added; if it is a liquid, 2 ml., or a larger volume, made about 10 N with respect to hydrochloric acid together with 2 ml. water may be used. Five ml. of 10 N hydrochloric acid are added from a buret and then 2 ml. of the purpurin solution from a pipet. Forty ml. of the cobalt-dichromate solution measured with a graduate are put into a similar oil-sample bottle and used to give standard color for comparison. The zirconium solution in hydrochloric acid is now added from a buret until the color of the solution begins to approach that of the cobalt-dichromate standard. More 10 N hydrochloric acid is then added to bring the total volume just under 40 ml., more zirconium being added till the color matches that of the standard with a total volume of 40 ml. (adjusted by adding sufficient 10 N hydrochloric acid from the buret). The zirconium solution must be added slowly with a shaking so that the titration requires at least 1 to 2 minutes.

The number of milligrams of zirconium used is calculated and 1 mg. subtracted from the amount.

Fluoride Corresponding to Zirconium Used

Zirconium Used Mg.[a]	Fluoride Present Mg.	Zirconium Used Mg.[a]	Fluoride Present Mg.	Zirconium Used Mg.[a]	Fluoride Present Mg.
1	0.40	10	4.15	19	8.90
2	0.75	11	4.65	20	9.50
3	1.20	12	5.10	21	10.10
4	1.60	13	5.60	22	10.72
5	2.00	14	6.12	23	11.40
6	2.47	15	6.63	24	12.08
7	2.90	16	7.15	25	12.90
8	3.25	17	7.73	26	13.70
9	3.70	18	8.26	27	14.53
				28	15.40

[a] Minus 1 mg.

Suppose that 8.75 mg. of zirconium were used in the titration. By interpolation it is found that 7.75 mg. of zirconium correspond to 3.16 mg. of fluorine.

Determination of Microquantities.—The method for titration of fluoride described cannot be used for titration of quantities of fluoride of less than 0.5 mg. A special colorimetric titration procedure is described below for amounts of fluorine between 0.01 and 0.05 mg.

The zirconium-purpurin reagent is prepared by adding slowly with shaking a solution of 9 mg. of purpurin in 30 ml. of ethanol to a solution of 0.16 gram of zirconium oxychloride in 6 N hydrochloric acid. Add 620 ml. of concentrated hydrochloric acid to the mixture, and make to 1 liter with water. The standard fluoride solution is a solution of sodium fluoride containing 2 mg. of fluorine per 100 ml. of 8 N hydrochloric acid.

Measure out 10 ml. of the zirconium-purpurin reagent into each of two test tubes of uniform diameter. Add the unknown sample made up to 2 ml. and 6 N with respect to hydrochloric acid to one test tube. To the other add 2 ml. of 6 N hydrochloric acid. Add about 2.4 ml. of the standard fluoride solution from the microburet to the second tube, which gives an orange color. Then add the same fluoride solution to the other test tube and enough 8 N hydrochloric acid so that the colors match when the volumes are the same.

The difference in the amount of standard fluoride added to both test tubes corresponds to the amount of fluorine in the unknown. Thus, if 2.4 ml. were used for the blank and 1.7 ml. for the sample, the fluorine content of the unknown is $(2.4-1.7)0.02=0.014$ mg.

The end point can be recognized within 0.1 ml. of the standard fluoride solution—that is, the method is accurate within 0.002 mg. of fluoride. Hence, the amount of fluoride in the sample should be 0.01 mg. or larger in order to get an accuracy of at least 10%. The upper limit of fluorine in the sample amounts to 0.05 mg. according to the procedure described. Larger quantities can be determined if larger tubes and more of the zirconium-purpurin reagent are used.

Interfering Substances.—Colored substances, substances forming chlorine with hydrochloric acid, substances precipitating with zirconium (phosphates) or forming more or less stable complexes with fluoride (aluminum, boric acid), and in addition, sulfates oxalates, and nitrites interfere with the titration. Successful titrations have been made in the presence of nitrates, sulfites, acetates, iodides, bromides, zinc, calcium, barium, magnesium and alkali salts.

Oxidizing substances can be reduced with sodium sulfite before the titration. Aluminum ions and boric acid tend to form complexes with fluoride. Since these complexes are less stable than the zirconium complex in the strong acid medium, titrations can be made in the presence of small amounts of these substances. In the titration of 2 mg. of fluoride 7.50 ml. of reagent were required; in the presence of 10 mg. of aluminum, 7.50; of 15 mg. 7.2; of 20 mg., 7.0; of 30 mg., 6.1; and of 50 mg., 5.5 ml., respectively. With the same amount of fluorine and 1 to 10 mg. of boric acid the results found were about 5% high. The complex formation does not interfere yet or at any rate is overshadowed by a tendency of boric acid to react with the zirconium-purpurin reagent. With 100 mg. of boric acid the results were 33% low. Phosphate interferes strongly; when as little as 1 mg. is present, it becomes impossible to titrate a 1-mg. sample of fluoride, owing to the cloudy appearance of the solution.

GALLIUM [1]

Ga, *at.wt.* **69.72;** *sp.gr.* **5.95;** *m.p.* **30° C.;** *oxide* **Ga_2O_3**

Occurrence.—Gallium is a very rare element. Until recently, it had only been found in traces in a large number of zinc blendes, iron ores, and aluminium minerals (bauxite and kaolin). The mineral germanite, discovered in South Africa in 1924,[2] contains 8.7% of germanium and 0.7% of gallium. In zinc smelting, gallium may concentrate in the retort residues, in the form of an indium-gallium alloy.

Uses.—Gallium melts at 30° and boils at about 1700° C. It has therefore come into use, in the form of gallium-in-quartz thermometers graduated to 1000° C., for the measurement of temperatures beyond the range of mercury-in-glass thermometers.

Behavior in Solution.—Gallium bears a decided resemblance to aluminum in its chemical reactions. Ammonia or ammonium sulfide precipitates the white hydroxide, which is a weaker base than alumina, hence more readily soluble in caustic soda; it is markedly soluble in ammonia, the solubility being increased by ammonium salts. Gallia is not quantitatively precipitated as basic acetate. The metal is not precipitated by hydrogen sulfide from acid or neutral solution, but adsorbed by the hydrogen sulfide precipitates of other metals in acid solution. Unlike aluminum, gallium is precipitated as a ferrocyanide insoluble in hydrochloric acid (1 : 2 water).

DETECTION

The minute quantities in which gallium occurs in minerals (with the single exception of germanite) call for a spectroscopic method as the surest means of detection, the spark spectrum of the element showing an intense violet line at λ 4170 and a less intense one at 4031. A spark of about 2 mm. is taken off the surface of the chloride solution, obtained according to the indications given below.

PREPARATION OF THE SOLUTION

It is necessary to take large quantities—at least 100 gms.—of the common ores for the determination. Blende is treated with aqua regia; the nitric acid

[1] Chapter by W. R. Schoeller, Ph.D., metallurgical chemist, London, England.
[2] Kriesel, Chem. Zeit., 48, 961, 1924.

is subsequently expelled by evaporation with hydrochloric acid. Iron and manganese ores are dissolved in strong hydrochloric acid, bauxite requires fusion with bisulfate, kaolin is fused with sodium carbonate and the silica removed from solution by the usual acid evaporation.

SEPARATIONS

(1) **From Bivalent Metals.**[3]—The solution, containing but little free mineral acid, is treated with excess of ammonium acetate, and ammonium nitrate so as to contain about 2% of the salt; it is then boiled and precipitated with a fresh 10% solution of tannin. The quantity of the latter should be 10 times that of the gallium, but not less than 0.5 gm. The bulky white gallium precipitate is collected and washed with dilute ammonium nitrate solution, containing a few drops of acetic acid, until free from chlorides. If at all substantial, it is dissolved in dilute hydrochloric acid, and reprecipitated by addition of ammonium acetate, nitrate, and tannin as before.

(2) **From Aluminum, Chromium, Indium, Uranium, Cerium.**[4]—The cold solution of the metals in 2 N sulfuric acid is treated with a 6% solution of cupferron until no further precipitation takes place. The white flocculent precipitate is collected under gentle suction. If cloudy, the filtrate is treated with 1 or 2 ml. of reagent and again passed through the filter containing the bulk of the precipitate, which is washed with 2 N sulfuric acid. The filtrate is kept under observation, and if a fresh cloudiness develops, another filtration is made. The washed precipitate should be free from chloride. If more than 2 gms. of alumina, or if more india than gallia, is present (in the latter case the precipitate will be yellow while hot), the precipitation should be repeated.

(3) **From Aluminum, Indium, and Iron.**[5]—Like ferric chloride, gallium chloride can be extracted by repeated shaking with ether from a 6 N hydrochloric acid solution. The extract is evaporated, and the residual liquid poured into boiling 0.3 N sodium hydroxide. The gallium goes into solution. The ferric hydroxide is filtered off and washed; the filtrate is acidified and precipitated with ammonia, or with ammonium acetate and tannin.

(4) **From Iron**[6] (*A*: More iron than gallium).—The cold sulfate solution, which should be free from ammonium salts, is approximately neutralized with sodium carbonate, and a solution of 10 gms. of sodium thiosulfate added. It is then heated, and kept boiling for 15 minutes, with additions of 10-ml. portions of aniline at intervals of 5 minutes; this completes the neutralization. The precipitate, which contains the gallia and a little iron, is collected, washed with hot water, and ignited. (*B*: More gallium than iron.) For the removal of the remaining iron, the ignited precipitate is fused with bisulfate, the solution treated with tartaric acid and ammonia, and the iron precipitated as sulfide. The filtrate is acidified with acetic acid, the hydrogen sulfide boiled off, and the

[3] Moser and Brukl, Monatsh. Chem., 50, 181, 1928; 51, 325, 1929; Brukl, *ibid.*, 52, 253, 1929.
[4] Moser and Brukl, *loc. cit.*
[5] Swift, J. Am. Chem. Soc., 46, 2375, 1924.
[6] Moser and Brukl, *loc. cit.*

gallium precipitated by boiling with tannin and ammonium acetate as explained under (1).

GRAVIMETRIC ESTIMATION

Gallium is always weighed as the oxide, obtained by ignition of the hydroxide, the tannin complex, or the cupferron precipitate. The washed precipitate is dried with the paper in a tared porcelain crucible. It is then heated on an asbestos mat till charring is over and ignited till white, finally over a blast burner. The oxide is hygroscopic, and should be weighed without delay. As gallium chloride is volatile, it is important that the precipitate should be washed free from chloride ion if this is present in the solution. Gallium precipitates should be ignited in porcelain; if platinum crucibles are used, partial reduction by diffusing burner gases may take place, with deterioration of the crucible.

Estimation in Base-Metal Ores.—The cold acid solution of a large quantity of the ore, obtained as explained before, is treated with zinc for the purpose of removing most of the heavy metals. The filtrate is then boiled with a large excess of zinc; the precipitate thus obtained consists of basic salts of iron, aluminum, gallium, and zinc.

(*a*) The precipitate is dissolved in hydrochloric acid, the iron oxidized with nitric acid, and the solution precipitated with ammonia. The precipitate is dissolved in 6 N hydrochloric acid, and the solution repeatedly extracted with ether. The ethereal extracts are evaporated, the residual solution evaporated with sulfuric acid, and the iron and gallium separated from each other according to " Separation from Iron, *A*."

(*b*) Alternatively the precipitate, if low in iron, is dissolved in 2 N sulfuric acid, for cupferron treatment (see " Separations (2) "). The resulting precipitate is fused with bisulfate and the iron precipitated as sulfide from ammoniacal tartrate solution (see " Separation from Iron, *B* ").

GERMANIUM

Ge, ***at.wt.*** **72.6;** ***sp.gr.*** **5.47;** ***m.p.*** **958;** ***oxides*** **GeO, GeO_2**

The element was predicted by Mendeleff and called by him "Ekasilicon." It was later discovered by C. Winkler in 1866 in the mineral argyrodite, $GeS_2 \cdot 4Ag_2S$. Its valences are 2 and 4, the latter being more common. It occurs in topaz, in certain zinc ores, and blendes and is occasionally associated with silver and tin sulfides, and in tantalum and niobium minerals.

Germanium dioxide forms a white powder of acid properties. Germanous oxide is a grayish powder. The tetrafluoride GeF_4 is similar to the tetrafluorides of carbon and silicon. The sulfide, GeS_2, is a white precipitate formed by action of H_2S on germanium solutions. The precipitate is soluble in ammonium sulfide, polysulfide and in ammonium hydroxide.

For details of detection reference is given to the work of Papish, Brewer and Holt, J. Am. Chem. Soc., **49**, 3028, 1927; J. H. Müller, J. Am. Chem. Soc., **43**, 2549, 1921; Wada and Kato, Sci. Inst. Phys. Chem. Research, **2**, 243, 1925.

ESTIMATION

The volatility of the tetrachloride of germanium (b.p. $GeCl_4$ 86° C.) makes it inadvisable to effect solution by the action of HCl or aqua regia. The mineral is decomposed by fusion with sodium carbonate and sulfur (1 : 1), and the melt extracted with water. A second fusion of the residue and re-extraction is advisable. The filtrate containing the germanium, etc., is neutralized with dilute H_2SO_4 and the solution further acidified until it contains about 25% free H_2SO_4[1] (i.e. is 5 N in respect to this acid). GeS_2 is precipitated from this solution by saturation with H_2S and settling for 10–12 hours to coagulate the almost colloidal precipitate. The sulfides are filtered off and washed with 5 N H_2SO_4 solution saturated with H_2S.[3]

SEPARATIONS

The sulfide of germanium, obtained as directed above, may be separated from Cu, Hg, Pb, Bi, Cd and Cu by dissolving with alkaline sulfide or polysulfide and filtering as in case with the separation of As, Sb and Sn.

[1] 9 N HBr is also satisfactory (Noyes and Bray, Qual. Anal. Rare Elements). The bromide is not volatile as is the chloride.

The volatility of the chloride affords a method of separation from a number of other elements.[2]

DETERMINATION AS OXIDE [3]

The sulfide obtained by precipitation of GeS_2 from a 5 N H_2SO_4 solution and washing with 5 N H_2SO_4 (saturated with H_2S) is dissolved in NH_4OH and filtered into a weighed large-sized crucible or dish of platinum. The residue is washed until the washings pass through uncolored. To the filtrate and washings about 25 ml. of 3% H_2O_2 are added and the solution evaporated and the residue heated to 105° C. This is now moistened with H_2SO_4 and heated to expel ammonium sulfate and free acid, and then ignited to constant weight and weighed as GeO_2.

DETERMINATION AS MAGNESIUM ORTHOGERMANATE [4]

The compound Mg_2GeO_4 is obtained by precipitation with magnesium sulfate from an ammoniacal solution. The precipitation does not occur in presence of ammonium tartrate. Phosphate and arsenate are precipitated under these conditions. (See also Qual. Anal. Rare Elements, Noyes and Bray.)

Procedure.—Germanium is precipitated as sulfide as described in the previous paragraphs. The precipitate is dissolved in NH_4OH and H_2O_2. The excess of the peroxide is expelled by boiling the solution. The solution of germanium is made faintly acid with H_2SO_4 and about 15 ml. of 4 N $(NH_4)_2SO_4$ solution added and 30 ml. of N $MgSO_4$ solution. Now NH_4OH is added until the free acid is neutralized and 20 ml. in excess. The solution is heated to boiling and then allowed to cool and settle for 10–12 hours. The precipitate is filtered and washed with dilute NH_4OH (1 : 10), using as little of the wash reagent as possible, 40–50 ml. The residue is ignited according to the procedure recommended for magnesium estimation and then ignited to constant weight and weighed as Mg_2GeO_4.

[2] L. M. Dennis and J. Papish, J. Am. Chem. Soc., **43**, 2139, 1921; L. M. Dennis and E. B. Johnson, J. Am. Chem. Soc., **45**, 1380, 1923.
[3] E. B. Johnson and L. M. Dennis, J. Am. Chem. Soc., **47**, 790, 1925.
[4] J. H. Müller, J. Am. Chem. Soc., **44**, 2493, 1922.

GOLD [1]

Au, *at.wt.* 197.2; *sp.gr.* 19.33; *m.p.* 1063; *b.p.* 2600° C.; *oxides*, Au_2O, Au_2O_3

Gold is commonly found in igneous rocks that are high in silica, in quartz veins, in sedimentary rocks and metamorphic rocks. It is found in placer deposits and in alluvial sands. It may occur alloyed with silver and is frequently found associated with bismuth, copper, lead and iron. It occurs combined as telluride, silvanite, gold and silver telluride; calaverite, gold telluride. Combined gold may be found in pyrite, chalcopyrite, galena, sphalerite, arsenopyrite, tetradymite. It occurs in sea water. In native state it is found in grains, scales, plates and nuggets.[2] The hardness of the metal varies from 2.5 to 3. The tellurides vary in color from silver white, yellow, steel gray to nearly black.

DETECTION

Because of the limited application and tediousness of wet methods, the detection of a small quantity (2 parts per million or less) of gold in a mineral or base metal is most positively carried out by furnace methods of assaying. Wet methods of detection of traces of gold can be applied only to solutions free of colored salts and elements precipitated by the reagents employed. As a rule, in the treatment of an unknown substance, advantage is taken of the solubility of most metals and their compounds, and insolubility of gold by one of the mineral acids.

Detection of Gold in Alloys.—In metals or alloys which produce colorless solutions with dilute nitric acid, gold, in the absence of other insoluble matter,

[1] On account of the conspicuous glistening yellow appearance of the native element, gold attracted the attention of man during the early ages and probably is the oldest known metal. The use of the metal for ornaments is mentioned in the Old Testament and the early writings of the Greeks and Romans. It still finds extensive use in jewelry and ornaments. Its non-corrosibility, ductility and beauty of color and luster have served to make the element valuable for many purposes—dental uses, foil for covering ornaments, finely spun wire, in the arts for decorative purposes.

[2] In Australia two nuggets were found weighing 184 and 190 pounds respectively.

exhibits itself as a black or brownish residue which settles readily, and from which the liquid can be separated by careful decantation. If unassociated with metals of the platinum group, this residue will become yellowish brown on heating with conc. nitric acid.

In copper, nickel and such alloys, which leave a residue of sulfur, carbon or silicious matter on treatment with dilute nitric acid, the solution is filtered through double ashless filters and the filter and residue incinerated in a porcelain crucible. The residue, which may require pulverizing, is digested for a few minutes with aqua regia, and the dilute, filtered solution evaporated to dryness by heating below 200° F. Just as soon as dry, the mass is moistened with the least quantity of hydrochloric acid and the purple of Cassius test applied to its water solution in a small volume. This test is made by adding a solution of stannous chloride, containing stannic chloride. In strongly acid and concentrated gold solutions a precipitate of brown metallic gold is obtained. If the solution is but slightly acid and dilute, a reddish purple color is produced by colloidal gold and the stannic acid. The tint fades on standing. Addition of ammonia produces a red coloration.

This test applied to 1 part of gold in 600,000 of solution will impart a perceptible shade; to double this quantity, a mauve color. When gold is present in somewhat greater proportion a flocculent precipitate will form.

Test for Gold in Minerals.—From minerals, in which the metal exists in unalloyed, or uncombined state, gold may be extracted by iodine in potassium iodide solution, or by chlorine or bromine water. All minerals containing sulfides should be roasted. In natural or roasted state the sample should be very finely pulverized, and usually yields the gold best if first digested with nitric acid and washed free of soluble salts. The sample in a flask is covered with bromine water, the flask closed with a plug and shaken frequently during a period of three or four hours. The purple of Cassius test is applied to the extract, removed by decantation after concentration.

If it is evident that base metals are present in the bromine water extract in quantity sufficient to mask the purple of Cassius test, hydrogen peroxide is added to the concentrated liquid, slightly alkaline with sodium or potassium hydroxide or carbonate.[3] After boiling the solution until hydrogen peroxide is removed, precipitated hydroxides or carbonates are dissolved by hydrochloric acid. Gold in exceedingly small quantity exhibits itself as a light-brown residue on a fine filter. This indication should be confirmed by a purple of Cassius test on the aqua regia solution of the residue; the test carried out in the same manner as on the residue from a solution of a metal.

Benzidine Acetate Tests.—Maletesta and Nola [4] make use of benzidine acetate (1 gram benzidine dissolved in 10 ml. acetic acid and 50 ml. water) as a reagent in the detection of gold and platinum in quite dilute solutions. Gold gives a blue coloration which gradually changes to violet. The coloration is green in the presence of free acetic acid, changing to blue with addition of benzidine in excess. Platinum gives a blue flocculent precipitate, the formation of which is promoted by heating. Free mineral acids have no influence on the gold and retard the platinum reaction only in the cold. Since ferric salts give a blue coloration, stable only in excess of benzidine, their absence must be assured

[3] Vanino and Seeman, Ber., 32, 1968, 1899; Rossler, Z. anal. Chem., 49, 733, 1910.
[4] Boll. chim. farm., 52, 461 (1913). C. A., 8, 1397 (1914).

before application of the test for the precious metals. The limit of sensitiveness of the test is 35 parts for gold and 125 parts for platinum per 10,000,000.

Phenylhydrazine Acetate Test.—E. Pozzi Escot [5] adds phenylhydrazine acetate to a very dilute gold solution which contains an excess of an organic acid (formic or citric). A violet coloration, permanent for several hours, is imparted. The depth of color is proportional to the quantity when the gold is present in less amount than one part in 500,000.

ESTIMATION

PREPARATION AND SOLUTION OF THE SAMPLE

Gold in massive form is practically insoluble in pure nitric, sulfuric or hydrochloric acid, but in the presence of oxidizing agents is attacked appreciably by sulfuric, and actively by hydrochloric acid. Gold is found in minute quantity in the nitric acid [6] solution of its alloys, and in such as contain selenium the amount may be a large part of the total present.

Gold is attacked energetically by aqua regia. Large amounts of gold are dissolved with requirement of least attention when the proportion of hydrochloric acid is several times that of the aqua regia formula (3HCl : $1HNO_3$).

Gold is dissolved by solutions of chlorine or bromine, by alkaline thiosulfates; in the presence of free oxygen by iodine in potassium iodide solution, by soluble cyanides, by fused potassium or sodium hydroxide; by fused potassium or sodium nitrate or sulfide. In a finely divided state, it is dissolved by a solution of potassium or sodium hydroxide.

Gold alloys quickly with molten lead. When in the form of bright, untarnished particles it alloys readily with mercury.

The methods generally employed for the determination of gold involve weighing of the metal. This is separated by wet and dry assay. A chapter is devoted to the latter procedure in this text. Gold may be precipitated from its solution by displacement by a more positive element or by reducing agents—SO_2, oxalic acid, ferrous sulfate, etc. The methods follow later in the chapter.

The element resists attack by single acids, but dissolves in a mixture of HCl and HNO_3—aqua regia.

SEPARATIONS

Gold is readily displaced from acid solution by means of base metals, aluminum, magnesium, zinc, etc. The insolubility of the metal in HCl, H_2SO_4 and HNO_3 when used singly effects a separation from the majority of common

[5] An. chim. anal. chim. appl., 12, 90, 1907; J. Soc. Chem. Ind., 26, 645 (1907).
[6] Dewey, J. Am. Chem. Soc., 32, 318 (1910); E. Keller, Bull. Am. Inst. Mining Eng., 67, 681.

metals. Gold is easily reduced by a number of reducing agents—sulfur dioxide gas, or solution, sulfites, ferrous sulfate, oxalic acid, dimethylglyoxime, etc.

Separation of Gold from the Platinum Group.[7]—The elements brought into solution with aqua regia and converted to chlorides by expulsion of HNO_3 by repeated evaporation with HCl are treated with SO_2. Gold precipitates, slightly contaminated by the other noble elements. The metal is dissolved in aqua regia, HNO_3 expelled by evaporation with HCl. The solution diluted is treated with HCl so as to contain 2–3 ml. HCl (sp.gr. 1.18) and 3–5 drops of H_2SO_4 (sp.gr. 1.84) per each 100 ml. of solution and gold precipitated by addition of oxalic acid, the solution boiled and filtered through a fine-grained filter containing paper pulp, and washed with dilute HCl. Further details follow under the gravimetric wet method given later in the chapter. Should the gold be contaminated with platinum or palladium the ignited metal will be colored markedly by these.

Separation of Gold from Tellurium.[8] Gold can be precipitated quantitatively by HNO_2 at a pH somewhat greater than 1, obtained by buffering 1.5% HCl solution with Rochelle salt. Gold is also precipitated quantitatively by $FeSO_4$ in the presence of 1–2% of HCl. The Te is not precipitated under these conditions.

GRAVIMETRIC METHODS

Gold is always weighed in metallic state, and is determined most accurately in the form of the mass obtained by dilute nitric acid treatment of the silver alloy resulting from the operation of cupellation in the method of assaying by furnace processes. On account of tediousness in making complete separation from associated metals, and of uncertainty in collection of the product in a form suitable for accurate weighing, direct precipitation methods are never used for the valuation of gold-bearing material, but may be applied to the estimation of gold in plating baths, the Wohlwill parting electrolyte and solutions of similar type.

Precipitation of Gold.—From such solutions of auric chloride, slightly acid with hydrochloric, freed of oxidizing agents by evaporation and displacement with hydrochloric acid, and containing but little of the salts of the alkalies or alkali earths, gold is separated from other than occluded platinum and palladium by precipitation with oxalic acid, ferrous sulfate, or hydrazine hydrochloride.

[7] For details of separation of gold from platinum metals by ether extraction consult article by F. Mylius, Z. anorg. allgem. Chem., 70, 203, 1911; for ethyl acetate extraction by Noyes and Bray, see also V. Lenher and C. H. Kav, J. Phys. Chem., 30, 126, 1926.

[8] Lenher, Smith and Knowles, Ind. Eng. Chem., Anal. Ed., 6, 43 (1934).

The reactions are hastened by heat. When salts of the alkalies or earths are present, equally good separation and more complete precipitation can be obtained by addition of excess of sodium peroxide, boiling vigorously for a few minutes and then acidifying with hydrochloric acid. The precipitated metal is collected on an ashless filter paper, and, after drying, weighed.

Gold precipitated from a very weak solution is in such fine form that it is not wholly retained by the finest paper.

WET GOLD ASSAY OF MINERALS

A wet gold assay, suitable for prospector's use,[9] is carried out by covering one assay ton (29.17 grams) of the finely pulverized natural or roasted ore in a porcelain mortar with 50 ml. of a solution of 2 parts of iodine and 4 parts potassium iodide in 100 ml. of water. Sulfide ores should be roasted and digested with nitric acid before treatment with the iodine solution. Similar treatment is advantageously applied to all ores. The ore is ground in contact with the iodine solution and additions of the halogen are made whenever the liquid becomes colorless. The solution is then allowed to stand at least an hour. To the filtrate and washings from the pulp, in a glass-stoppered bottle or flask, are added 5 grams of gold-free mercury. The liquid is shaken vigorously with the mercury until clear. The mercury is then transferred to a small porcelain casserole, washed with clean water and dissolved by warming carefully with 10 ml. nitric acid. The gold mass is washed free of nitrate of mercury by decantation, dried and annealed by heating in a casserole over a Bunsen flame, and the metal weighed. Each milligram represents an ounce per ton. Results obtained by this method of assaying are usually more than 50% of the actual gold content.

Electrolytic Method.—The gold content of a cyanide plating bath containing no potassium ferrocyanide may be estimated by electrolysis.[10]

Procedure.—A measured quantity, 25 to 50 ml. in a tared platinum dish, is diluted to 1 cm. of the rim of the dish and, using a carbon or platinum anode, electrolyzed for about three hours at a current density $ND_{100}=0.067$ amp. (0.0043 per square inch). Completion of deposition is recognized by the lack of any deposit within fifteen minutes, on a platinum strip suspended on the rim of the dish. The dish plus gold deposit is washed, rinsed with alcohol, dried at 212° and when cold weighed.

The following is a summary of the conditions of deposition of gold in compact form as described by Classen:[11] 3 grams potassium cyanide were added to a gold chloride solution containing 0.0545 gram of gold in 120 ml. This solution heated to about 55° C. when electrolyzed at a current density of $ND_{100}=0.38$ amp. (0.024 amp. per square inch), with a potential difference of 2.7–4.0 volts, deposited its gold content in one and a half hours. Time required for deposition is tripled if the electrolyte is at room temperature.

Miller[12] deposited 0.1236 gram of gold in two and a quarter hours from 125 ml.

[9] De Luce, Mining Sci. Press, 100, 895 (1910); Hawson, Mining Sci. Press, 100, 936 (1910); Davis, Mines and Minerals, Oct. 1910, Feb. 1911; Austen, Inst. of Mining and Met., May 31, 1911.

[10] Electro Deposition of Metals, Langbein.

[11] Classen, "Quantitative Chemical Analysis by Electricity," Classen-Boltwood.

[12] J. Am. Chem. Soc., 26, 1255 (1904).

of electrolyte at 50° C. containing 1 gram potassium cyanide by a current of $ND_{100} = 0.03$ amp. (0.002 amp. per square inch) and 2.5 volts.

Perkin and Preble [13] use an electrolyte containing ammonium thiocyanate in place of potassium or sodium cyanide.

Gold is removed from the platinum electrode by warming with a solution of chromic anhydride in a saturated salt solution [14] or with a solution of potassium cyanide containing some oxidizing agent as hydrogen peroxide, sodium peroxide or alkali persulfate.[15]

Sulfur Dioxide-Oxalic Acid Method.—The separation of gold from almost all metals except selenium, tellurium, lead and the alkaline earths is effected by the following procedure: .

The solution containing preferably 0.5–1.0 gram of gold is acidified so as to contain not over 5 ml. HCl (sp.gr. 1.18) per 100 ml. of solution and to each 100 ml. are added 25 ml. of a saturated solution of SO_2. The solution is allowed to stand on a steam bath for one hour and 5–10 ml. more of SO_2 water added. The solution is allowed to cool; it should still smell of SO_2. The contents are poured through a close-grained filter containing filter paper pulp after washing several times by decantation with dilute HCl (1 : 99) and finally on the filter, the acid being hot. Should the platinum group be present a further separation is advisable. The gold is dissolved in dilute aqua regia (8 ml. HCl, 2 ml. HNO_3 and 10 ml. H_2O per each gram of gold or less). The gold is filtered from the paper pulp and the pulp washed thoroughly with dilute, hot HCl. The extract is evaporated to dryness, 2–3 ml. HCl added and the evaporation repeated and this repeated a second and third time to expel HNO_3. The residue is taken up with 5 ml. HCl, 5 drops of H_2SO_4 and 75 ml. H_2O per each gram or less of gold present. The solution is treated with 25 ml. of a saturated solution of oxalic acid per each 75 ml. of solution and boiled 10–15 minutes. Now 5–10 ml. of saturated oxalic acid solution are added, the solution again boiled, and allowed to stand for about four hours, then filtered through a fine-grained ashless filter containing ashless filter paper pulp. The gold is washed with very dilute HCl (1 : 99) and ignited and weighed as metallic gold.

VOLUMETRIC METHODS

These methods are applicable to the determination of the strength of chloride of gold solutions used in photography, electro-gilding, and as electrolyte in the Wohlwill parting process.

Preparation of the Sample.—Nitric acid or nitrates in the solutions should be removed by repeated evaporations to syrup with addition of hydrochloric acid

[13] Elec. Chem. and Met. Ind., 3, 490.
[14] Classen-Boltwood, "Quantitative Chemical Analysis by Electricity."
[15] Rose, "Metallurgy of Gold," 5th Ed., 469.

saturated with chlorine. Free chlorine or bromine should be removed by addition of ammonia to formation of permanent precipitate, then making the solution very slightly acid with hydrochloric acid and heating until the precipitate of fulminating gold dissolves. The gold solution should contain but little free hydrochloric acid, an excessive amount of which may be removed by ammonia.

PERMANGANATE METHOD

Weak gold solutions should be concentrated whenever possible. The permanganate method,[16] which is not applicable when the sample contains organic matter, depends upon the titration, after complete precipitation of gold, of the unoxidized portion of a measured quantity of an added reagent of a known gold precipitating value. The reagent may be ammonium or potassium oxalate, ferrous sulfate or ferrous ammonium sulfate in solutions varying from 5 to 25 milligrams gold precipitating value and is titrated with a permanganate solution of approximately equal oxidizing strength. One part of gold requires for precipitation 1.08 of ammonium oxalate, 1.40 of potassium oxalate, 4.22 of ferrous sulfate, 5.96 parts ferrous ammonium sulfate, each in crystalline form. The most satisfactory precipitations are made with the iron salts. The standard solution of either should contain about 0.1% of sulfuric acid. One part of gold, in solution as auric chloride, has an oxidizing value equivalent to 0.4808 part of potassium permanganate.

The precipitating value of 0.2548 gram of dry Sorenson's sodium oxalate is 250 milligrams of gold, and by titrating a solution of this amount of oxalate in 250 ml. of water, acidulated with a few drops of sulfuric acid, the oxidizing value of the permanganate solution is obtained in terms of gold.

The value of the precipitating reagent and relative oxidizing value of the permanganate solution can be checked very accurately by adding a measured quantity of the reagent to an excess of gold chloride, filtering, washing thoroughly, incinerating and weighing the precipitate obtained in a tared porcelain crucible.

Procedure.—In carrying out the determination of a gold solution, a measured or weighed portion is freed of oxidizing agents, a measured amount of the standard precipitating reagent added in slight excess of the amount required to decolorize the solution, and digestion on a steam bath or hot plate continued until the gold settles out, leaving a clear liquid. A few drops of sulfuric acid may be then added and, without filtering, titration performed. The gold value of the quantity of reagent added, minus that found of the excess of reagent, is the gold content of the amount of the sample taken.

IODIDE METHOD

Small quantities of gold are determined by Gooch and Morley's iodide method.[17] A measured or weighed portion of the gold solution is treated,

[16] Boll. chim. farm., 30 (3), 35 (1894); Oesterr. Z. Berg.- u. Hüttenw., 182 (1880); Sutton, "Volumetric Analysis," 10th Ed.; E. A. Smith, "Sampling and Assaying of Precious Metals"; Mining Eng. World, 37, 853 (1913).

[17] Amer. Jour. Sci., 261 (1899); Mining and Eng. World, 37, 853 (1913); "Volumetric Analysis," Sutton, 10th Ed.; "Sampling and Assaying of Precious Metals," E. A. Smith.

as has been described for removal of oxidizing agents, with an excess of free hydrochloric acid. Potassium iodide solution is run into the cold liquid until the gold precipitated as aurous iodide is completely dissolved. Starch solution is then added, and the amount of N/1000 thiosulfate required to decolorize the liquid noted. From this amount is deducted the amount of N/1000 iodine required to just produce a perceptible rose tint in the liquid.

The reactions involved are $AuCl_3+3KI=AuI+I_2+3KCl$ and $I_2+2Na_2S_2O_3=2NaI+Na_2S_4O_6$.

The gold value of the N/1000 solution of sodium thiosulfate should be determined by performance of the operations of the method on a known quantity of gold, similar in amount and contained in a volume of solution approximately equal to that of the analysis.

Lenher's Method.—By Lenher's method [18] of determining gold in solutions free of oxidizing agents, sulfurous acid of a reducing strength of 2–5 milligrams gold per ml. is used as the reagent. The sulfurous acid requires frequent standardizing by means of standard iodine or potassium iodide to which a definite amount of standard permanganate has been added or by a gold solution of known strength. Using starch as indicator, the iodine liberated by addition of potassium iodide can be titrated by sulfurous acid. Bromine liberated by potassium bromide according to the equation, $AuCl_3+2KBr=AuCl+2KCl+Br_2$, can be titrated by sulfurous acid. Excess of magnesium or sodium chloride gives to auric chloride a yellow color which by sulfurous acid can be titrated to the colorless or aurous state. These alkaline salts do not interfere in the potassium bromide or iodide reactions.

COLORIMETRIC METHODS

Practical application of these methods is made in the estimation of gold in the liquors produced in the treatment of ores by the cyanide process.

PRISTER'S METHOD

By Prister's method [19] a slight excess of copper solution is added to a 100- to 200-ml. portion of a cyanide solution in which the cyanide has been decomposed by boiling several minutes after acidifying with hydrochloric acid. Assurance of the presence of an excess of copper is made by spot test with a solution of potassium ferrocyanide.

[18] J. Am. Chem. Soc., 35, 735, 1913.
[19] J. Chem., Met. and Mining Soc. Africa, 4, 235, 1904.

The copper solution is made by boiling for ten minutes in contact with copper shavings, a solution of 1 part blue vitriol and 2 parts salt in 10 parts of water, and adding a little acetic acid on cooling. A few drops of a 1 to 2% sodium sulfide solution are added, the liquid boiled for five minutes, the precipitate allowed to settle, and liquid separated by decantation onto a filter. The precipitate in the beaker and on the filter is dissolved with 2½ to 3 ml. of a 3 to 5% solution of potassium cyanide to which a few drops of potassium hydrate solution have been added.

Gold is precipitated from this cyanide solution (which may be turbid), by addition of 1 to 2 grams of zinc dust and warming to 100° F. for half an hour. Liquid is separated by decantation through a filter. The residue on the filter and in the beaker is first treated with hydrochloric acid to dissolve zinc, then with 10 ml. aqua regia, the reagent being passed several times through the filter. Stannous chloride solution is then added to the liquid diluted to 20 ml. Comparison of the coloration produced is made with that from a standard solution of gold treated in the same manner.

Cassel's Method.—By Cassel's method [20] 0.5 gram potassium bromate is mixed with 10 to 50 ml. of the cyanide solution and concentrated sulfuric acid added gradually with constant agitation until reaction commences. When the reaction stops, a saturated solution of stannous chloride is added dropwise until the liquid is just colorless. The tint produced is compared with that from a standard gold solution treated in the same manner.

Moir's Method.—By Moir's method [21] a measured quantity of the cyanide solution is oxidized by addition of 1 to 2 grams of sodium peroxide and boiling. If sufficient sodium peroxide is present, the brown spot produced by addition of a few drops of lead acetate will immediately dissolve. The lead-aluminum couple formed by addition of aluminum powder precipitates gold, which is filtered off. To the aqua regia solution of the precipitate a solution of stannous chloride is added drop by drop until the liquid is dissolved. The purple of Cassius tint developed is compared with permanent standards composed of mixtures of solutions of copper sulfate and cobalt nitrate which have been adjusted to shades corresponding to those produced by known amounts of gold treated according to the method described.

Bettel [22] filters suspended matter from the cyanide solution, adds a measured quantity of a strong solution of potassium cyanide which contains some cuprous cyanide and precipitates gold by the copper zinc couple produced by addition of a measured quantity of zinc fume. The remainder of the method is the same as Prister's.

Dowsett's [23] factory test of barren cyanide solutions is capable of detecting variation in gold value of 1 cent per ton in solutions varying from one cent to about 15 cents per ton. To 500 ml. of the sample in a bottle with slight shoulder are added 10–15 ml. saturated sodium cyanide solution, 2 or 3 drops saturated lead nitrate solution and 1–2 grams 200-mesh fine zinc dust. The stoppered bottle is shaken violently until the precipitate settles rapidly.

[20] Eng. and Mining J., Oct. 31, 1903.
[21] J. Chem., Met. and Mining Soc. S. Africa, Sept. 1913.
[22] Mining Eng. World, 33, 102 (1909); 35, 987 (1911).
[23] Trans., Inst. Mining Met., 22, 190 (1912–13); Chem. and Met. Eng., 12, 460 (1914).

Inverting the bottle allows the precipitate to settle into a casserole. Clear liquid is removed by decantation. Zinc is dissolved by hydrochloric acid added drop by drop until reaction ceases. A few drops excess hydrochloric acid and 3–5 drops dilute nitric acid (sp.gr. 1.18) are added and the liquid concentrated to 1–2 ml. The solution is transferred to a ½-in. diameter test-tube, about 1 ml. of stannous chloride reagent added and grade of cyanide solution estimated by the tint obtained after one or two minutes standing. 1/1000 oz. gold per ton of original cyanide solution gives a very slight coloration; 15/10000 a slight yellow; 1/500 a slight pinkish yellow; 3/1000 a strong pink; 1/250 the purple of Cassius. Too much nitric acid hinders the production and the presence of mercury causes modification of the color. No more lead nitrate should be used than is sufficient to produce a rapidly settling precipitate. The stannous chloride reagent is a water solution containing about 12½% crystals and 10% concentrated hydrochloric acid.

PREPARATION OF PROOF GOLD

Commercial gold may contain arsenic, antimony, selenium, tellurium, copper, lead, mercury, silver, zinc, palladium, platinum and other metals of the platinum group. The method of making pure gold depends to a certain extent upon the character and quantity of impurities.[24] The method described assumes the raw material to be of extreme impurity. The metal is treated in 10-gram portions.

When the metal contains silver its solution is effected most quickly by rolling extremely thin and annealing before treatment with acids.

The strips, in a covered No. 6 casserole on a steam bath, are dissolved with a mixture of 5 ml. nitric and 50 ml. hydrochloric acid. If but little silver is present the quantity of hydrochloric acid may be decreased to 25 ml. The solution is evaporated to dryness and the casserole gently heated over a Bunsen flame until all the gold is reduced to metal.

Digestion with ammonia will dissolve most of the silver and copper. After decanting the ammoniacal solution and washing with water, the gold is digested with hot nitric acid. If the solution is wine colored the digestion is continued for several hours, and reheated with fresh portions of acid until the absence of color indicates removal of palladium. The gold is now dissolved with 5 ml. of nitric and 15 to 20 ml. hydrochloric acids, evaporated to dryness, residue moistened with the least quantity of hydrochloric acid, dissolved with about 800

[24] Eng. and Mining J., 68, 785, 1899; "Metallurgy of Gold," Rose, 5th Ed.; Min. and Sci. Press, Nov. 14, 1903; "Manual of Fire Assaying," Fulton; "Assaying of Precious Metals," Smith.

ml. water and liquid transferred to a 1000-ml. beaker. After the faint cloud of silver chloride settles to the bottom of the beaker, the clear liquid only is siphoned to another beaker, and allowed to stand another period of several days if it appears at all cloudy. The clear liquid is now siphoned into a 1000-ml. flask and sulfur dioxide gas passed until the gold is practically all precipitated. The gold is allowed to settle, digested with hot nitric acid for a few minutes, washed by decantation several times, redissolved with aqua regia, solution transferred to a casserole, and nitric acid expelled by repeated evaporation to syrup with addition of hydrochloric acid. The product of the second evaporation is moistened with the least quantity of hydrochloric acid, dissolved with water and solution transferred to a 1000-ml. beaker or Erlenmeyer flask. To the liquid of about 500-ml. volume are added 11 grams of ammonium oxalate crystals. The beaker is permitted to remain on a steam bath until reaction is complete. The spongy mass of gold is now washed with hot water by decantation until free of salts.

The gold is dried, melted in a clay crucible which has previously been thinly glazed with borax glass and poured out into a mold of charcoal, graphite and clay or iron polished with graphite.

The ingot, which will have a volume of half a milliliter, is cleaned by paring with a knife and rolled or hammered into a thin sheet. The rolls or hammer should be clean, bright and free of grease.

The gold, cut into convenient strips, is digested for several hours with hydrochloric acid and finally washed thoroughly with distilled water.

The dried gold thus prepared may be considered 1000 fine.

FURNACE METHODS OF ASSAY FOR GOLD

Details of assay for gold and silver by furnace methods will be found following the chapter on Silver.

A considerable portion of this chapter was contributed by W. G. Derby, who for many years was connected with the Nichols Copper Company as assayer and research chemist.

HYDROGEN

H, *at.wt.* 1.008; *sp.gr.* 0.07; *b.p.* −253° C.; *m.p.* −259° C.

Hydrogen occurs free in small quantities in gases of volcanoes, and certain petroleum and gas wells. It occurs as a decomposition product in the decay of organic matter. It is found in traces in the atmosphere. With these exceptions practically all hydrogen in nature is found combined with oxygen in the form of water. The chemist is called upon to determine hydrogen in illuminating and fuel gas. A chapter is devoted to gas analysis in Volume II, where details for hydrogen determination in gases are given.

The determination of hydrogen in organic compounds in combined state and in iron, alloys, etc., in its occluded and loosely combined form is accomplished by oxidation to water with subsequent absorption and weighing as such. See the chapter on Carbon.

DETECTION

The lightness of the gas, its combustibility with oxygen with formation of water and its union with chlorine to form hydrogen chloride are methods for its detection in gas. Its detection and estimation in solid materials by oxidation to water necessitates the removal of free and combined water previous to the tests for hydrogen, or a separation of water from the gas before oxidation of the gas. Palladium is used for direct absorption of the gas. Details of the procedure are given in Volume II in the chapter on Gas Analysis.

Although various types of combustible gases were known to the alchemists, hydrogen was not definitely proven to be a distinct element until 1766 when Cavendish established its identity. The element was further studied by Lavoisier, from whom it obtained the name hydrogen, water producer.

The value of hydrogen in fuel and illuminating gas is generally known. In form of atomic hydrogen its efficiency for producing a welding gas is greatly increased. Its lightness has led to its use in balloons and dirigibles (1000 cubic feet of hydrogen will lift 700 pounds). It is used for the hydrogenation of fats (more than 350,000,000 pounds of solid fat produced from liquid fats per year); it is used in the conversion of coal into petroleum products by its removal of oxygen and building up of the hydrogen content; it is used in the production of ammonia (Haber-Bosch method). It is valuable in the commercial laboratory as a reducing agent.

An interesting (S. L. C.) universal indicator, made by the Synthetical Laboratories of Chicago, enables one to determine the pH value from 1.2 to 13.

A chart showing color changes of the indicator is used for comparison in place of buffered solutions as standards.

The color changes from pink pH 1.2 to brownish yellow pH 5, canary yellow pH 6.5, green pH 7.6, lavender pH 10 to purple pH 12–13.

DETERMINATION OF HYDROGEN IN STEEL

The method is based upon the oxidation of hydrogen liberated from steel by heat in presence of a current of oxygen. The water formed is absorbed and weighed.

Procedure.—Preliminary test. The apparatus is set up as shown in detail in Fig. 54. The heat is turned on and the oxygen gas passed through the silica

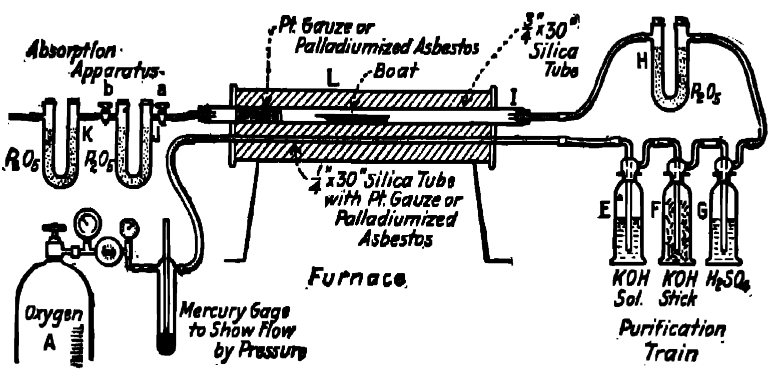


FIG. 54. Apparatus for Determining Hydrogen.

tube I, heated to redness (850° C.) at the rate of 100 ml. per minute, this rate having been established by a preliminary test noting the rate of bubbling through the acid in G and the pressure in C with the desired volume per minute. The gas is purified by passing through D, E, F, G and H, any hydrogen present being decomposed in the preheated tube D. Proceed now as follows:

Allow the gas to pass through the system for 5 to 10 minutes, disconnect the tube J after turning off the cocks " a " and " b " in the order named. Place in the balance case for 5 minutes, then open and close " b " rapidly. The oxygen in J will be at atmospheric pressure and at the temperature in the balance. Now weigh. Replace the tube again in the train, open the cocks " a " and " b " and continue the flow of oxygen for another 10 minutes. If there is an increase in weight repeat the test a third time, noting the increase of weight during a 30-minute run. This is the blank that must be deducted from the regular run. It should not exceed 1 milligram.

The Test.—Place in a clay boat previously ignited in a current of oxygen, or in a platinum boat containing ignited alundum powder, 10 to 30 grams of

steel in as large pieces as possible (hydrogen is liberated by drilling so that it is best to use the metal in strips or in a single piece). Insert the boat in the tube and quickly connect up the apparatus.

Turn on the oxygen at the rate of 100 ml. per minute and continue the flow for 30 minutes. Disconnect (after turning off cocks "a" and "b") the absorption tube J. Place in balance case as before and equalize the pressure by opening the cock "b" for an instant. Weigh. The increase of weight, minus the blank, is due to the water formed. This weight multiplied by 0.111 gives the hydrogen of the sample.

NOTES.—The blank is derived from the oxidation of the rubber connections, and this should be determined and deducted from the regular run.

It is not necessary to burn all the metal to oxide to eliminate the hydrogen. A 30-minute run is sufficient.

The P_2O_5 is placed in the tubes interspersed with glass wool; otherwise the tubes would pack, preventing the passage of the gas.

Testing Gas Apparatus for Leaks.—Connections between the parts of the gas apparatus, stop cocks, etc., should be tight to avoid intake or loss of gas, thus causing an error. The following simple method for testing for leaks is applicable to apparatus for the volumetric determination of gas as well as testing the tightness of combustion trains.

Procedure.—Close one end of the train. To the other attach a Hempel gas burette with two-way stop cock and connected to a reservoir of water. Open the two-way cock to the air and raise the reservoir until half of the gas in the tube is expelled. Now turn the cock to open a passage to the combustion train (or gas apparatus). Have the level of the water in the reservoir and the burette the same and note the exact reading. Now raise the reservoir about 10 inches; the gas will be under pressure. Lower the reservoir to its former position, levelling the water. If the level in the Hempel tube has risen an outward leak is indicated. See Fig. 54.

Now lower the reservoir to the table and after a few minutes raise to the first position. After levelling the water as before note whether the level has dropped in the Hempel. If so the apparatus leaks under reduced pressure.

Isotopes of Hydrogen.—Subsequent to the announcement of the spectral evidence for the existence of heavy hydrogen, or deuterium, D, the isotope of mass 2, in 1932,[1] a vast amount of work has been done on the properties of deuterium and its compounds. There is also evidence that a third isotope exists in very minute concentrations in water and other sources of hydrogen.

The analytical chemistry of hydrogen, deuterium, hydrogen deuteride and other deuterium compounds is in part based on physico-chemical methods—spectrographic; refractometric; mass spectrographic; thermal conductance; specific gravity either of the oxide or of the element. Organic compounds are burned to form water and deuterium oxide, and the density of the mixture enables one to estimate the relative numbers of atoms of hydrogen and deuterium in the compound.[2]

[1] Urey, Brickwedde and Murphy, Phys. Rev., 39, 164, 864 (1932).

[2] A summary of the important analytical methods is given by A. Farkas, Orthohydrogen, Parahydrogen and Heavy Hydrogen, Cambridge University Press, 1935. H. Erlenmeyer and associates give practical details for the estimation of deuterium in organic substances, Helv. Chim. Acta, 19, 129 (1936); 18, 1464 (1935).

INDIUM[1]

In, *at.wt.* 114.76; *sp.gr.* 7.12; *m.p.* 155° C.; *oxide* In_2O_3

Occurrence.—Indium is a rare element found in minute quantities in many deposits of zinc blende, in some tungsten and most tin ores, and sometimes in pyrites, siderite, and galena. It is sometimes found concentrated as an indium-gallium alloy of low melting-point in residues from zinc retorts.

Behavior in Solution.[2]—Indium, like gallium, resembles aluminum in its behavior. The pale yellow sesquioxide is obtained by ignition of the hydroxide, precipitated by ammonia from indium solutions: ammonium salts need not be added, and an excess of ammonia is immaterial as it has no solvent effect upon the precipitate. Indium is not completely precipitated as basic acetate, but quantitatively as a yellow sulfide by hydrogen sulfide from solutions containing acetic acid and ammonium acetate. Quantitative precipitation of the sulfide is also achieved in 0.03 to 0.05 N hydrochloric acid solution.

DETECTION

For the detection of indium in an ore, e.g., in zinc blende, the mineral is dissolved in hydrochloric acid with the addition, if necessary, of a little nitric acid, the excess of which is expelled by boiling with hydrochloric acid. Digestion of the filtered solution with metallic zinc precipitates all the indium together with lead, copper, cadmium, etc. The precipitate is dissolved in nitric acid and the solution evaporated with sulfuric acid to fumes. The mass is taken up with water and the lead sulfate filtered off. The filtrate is treated with ammonia, boiled, and filtered. The precipitate is dissolved in the minimum of hydrochloric acid, the solution neutralized with ammonia, an excess of sodium bisulfite added, and boiling continued for some time. A white microcrystalline precipitate indicates indium. As a confirmatory test the precipitate is dissolved in a few drops of hydrochloric acid, and a platinum wire is dipped into the solution and held in the Bunsen flame. A bright blue color, showing two characteristic bright blue lines (λ 4511.55 and 4101.95) when viewed through the spectroscope, confirms the presence of indium.

[1] Chapter by W. R. Schoeller, Ph.D., and A. R. Powell, Metallurgical Chemists, London, England.

[2] Moser and Siegmann, Monatsh. Chem., 55, 14, 1930.

PREPARATION OF THE SOLUTION

As indium only occurs in minute amounts in ores of other elements, it is necessary to employ the procedure indicated by the nature of the material under examination.

SEPARATIONS[3]

(1) **From Iron.**—The solution is treated with ammonia drop by drop until a precipitate begins to appear; this is dissolved in a minimum quantity of 0.1 N hydrochloric acid. The resulting acidity should be less than 0.05 N. Hydrogen sulfide is passed for 2 hours at 70° C., and the precipitate washed with hydrogen sulfide water barely acidified with hydrochloric acid. Large amounts of ferric salt are first reduced with hydrogen sulfide in acid solution; this is boiled under carbon dioxide for the removal of the gas, and neutralized after cooling.

(2) **From Aluminum.**—Indium is precipitated as sulfide from acetate solution treated with sulfosalicylic acid (which converts aluminum into a stable soluble complex), then neutralized with ammonium carbonate against methyl orange, and acidified with a little acetic acid. If the solution is too dilute, the indium sulfide does not flocculate readily.

(3) **From Manganese.**—In this case, indium is precipitated as sulfide from an acetate solution prepared as follows: mineral acid is first neutralized with ammonia; the solution is then treated with 30 ml. of 2 N acetic acid and 10 ml. of 2 N ammonia per 100 ml., heated to boiling, and subjected to a stream of hydrogen sulfide till cold.

(4) **From Zinc.**—The weakly acid solution is treated with six times as much ammonium chloride as the zinc present. After addition of methyl orange the solution is treated with 10% potassium cyanate solution until the indicator turns yellow, and gradually heated to boiling. The dense precipitate of indium hydroxide is collected and washed. If zinc largely predominates, the precipitate is dissolved in dilute hydrochloric acid, the solution neutralized with ammonia, and the precipitation repeated.

(5) **From Gallium.**—See chapter on Gallium.

GRAVIMETRIC ESTIMATION

(1) **As Oxide.**—Indium hydroxide precipitates, if formed in chloride solution, should be washed very thoroughly as indium chloride is volatile. The filter containing the hydroxide precipitate is dried in a tared porcelain or silica crucible and ignited gradually, finally over a blast burner for 15 minutes. The

[3] Moser and Siegmann, *loc. cit.*

oxide is not volatile at the temperature reached, and is not hygroscopic after strong ignition. Factor for In, 0.8270.

(2) **As Sulfide.**—The sulfide precipitate is washed with weak ammonium acetate solution, dried, heated to 350° C. in a stream of hydrogen sulfide, cooled in the same, and weighed as In_2S_3. Factor for In, 0.7047.

Estimation in Zinc Blende, Retort Residues, etc.—It is advisable to take as much as 100 gms. The procedure follows the lines of that described above under "Detection" with the usual precautions to render the separations quantitative. The accuracy of the estimation by precipitation with excess of sodium bisulfite is at least questionable. The following alternative procedure is therefore suggested, though an opportunity to test it in actual practice has not yet presented itself.

The solution of the blende in hydrochloric acid, with the addition of a little nitric acid if necessary, is filtered and boiled with metallic zinc till nearly neutral. The precipitate is collected, dissolved in hydrochloric acid (and chlorate if required), and copper and bismuth precipitated from the boiling solution with iron wire. The filtrate is again boiled with zinc, and the precipitate digested with nitric acid to eliminate tin. The filtered solution is evaporated to fumes with sulfuric acid, and the lead sulfate filtered off. The last filtrate is precipitated with ammonia and filter pulp, the precipitate dissolved in hydrochloric acid, and the precipitation repeated. This precipitate is again dissolved in hydrochloric acid, the acidity adjusted to less than 0.05 N, and the indium precipitated as sulfide as described under "Separation from Iron." The yellow sulfide is either weighed as such, or converted into and weighed as oxide after solution in nitric acid and precipitation with ammonia (see "Gravimetric Estimation").

IODINE [1]

I, *at.wt.* **126.92**; *sp.gr.* **4.948**$^{17°}$; *m.p.* **113.5°**; *b.p.* **184.4° C.**; *acids*, **HI, HIO, HIO_3, HIO_4**

Iodine is less common than the other members of the halogen group. It is found in a few rare minerals such as the iodides of copper, lead and silver; the iodate of calcium, " lautarite," occurs in Chili saltpeter, hence is a common contaminant of crude nitric acid. The element is found in some mineral waters; it occurs combined in sea water in form of iodides and iodates, hence occurs in sea plants. Drift kelp, laminaria digitata and laminaria stenophylla are important sources of iodine, as well as the mother liquor from the Chilian nitre works, the chief source of iodine. Free iodine, potassium iodide, and iodoform are important commercial products.

DETECTION

The element may be recognized by its physical properties. It is a grayish-black, crystalline solid, with metallic luster, brownish-red in thin layers. It vaporizes at ordinary temperatures with characteristic odor. Upon gently heating the element the vapor is evident, appearing a deep blue when unmixed with other gases, and violet when mixed with air. It colors the skin brown. Chemically it behaves very similarly to chlorine and bromine.

Free iodine colors water yellow to black, carbon disulfide violet, ether or chloroform a reddish color, cold starch solution blue.

Tannin interferes with the usual tests for iodine, unless ferric chloride is present.

Iodide.—The dry powder, heated with concentrated sulfuric acid, evolves violet fumes of iodine. Iodine is liberated from iodides by solutions of As^5, Sb^5, Bi^5, Cu'', Fe''', Cr^6, $H_3Fe(CN)_6$, HNO_2, Cl, Br, H_2O_2, ozone.

Insoluble iodides may be transposed by treatment with H_2S, the filtered solution being tested for the halogen.

Iodate.—The acidulated solution is reduced by cold solution of SO_2, or $K_4Fe(CN)_6$ (acidulated with dilute H_2SO_4), or by Cu_2Cl_2, H_3AsO_3, $FeSO_4$, etc.

[1] The observation of Courtois (1811) of the effect of ashes of sea weeds in corroding copper kettles and the liberation of a violet-colored gas by the action of sulfuric acid on the ash led to Gay-Lussac's work in isolating the element (1813). The value of iodine for medical purposes as an antiseptic and for relieving inflammation, its use in treatment of goitre and in laboratory operations are well known.

An iodate in nitric acid may be detected by diluting the acid with water, adding starch solution, then hydrogen sulfide water, drop by drop, a blue zone forming in presence of the substance.

ESTIMATION

In the determination of iodine it should be recalled that although the majority of its compounds are soluble in water, the iodides of lead, mercury, silver and palladium are difficultly soluble. In their presence special provision is made to obtain solution of the sample in iodine determinations. Free iodine is but slightly soluble in water, comparatively soluble in presence of potassium iodide, and soluble in alcohol. The element is volatile, so that care must be exercised in its determination in concentrated solutions, in which it occurs free. Decomposition of the sample is given in the section following.

PREPARATION AND SOLUTION OF THE SAMPLE

In dissolving the substance it will be recalled that free iodine is soluble in alcohol, ether, chloroform, glycerol, benzol, carbon disulfide, solutions of soluble iodides. One hundred ml. of water at 11° C. is saturated with 0.0182 gram iodine, at 55° C. with 0.092 gram.

Iodides of silver, copper (cuprous), mercury (mercurous), and lead are insoluble, also TlI, PdI_2. Iodides of other metals are soluble; those of bismuth, tin, and antimony require a little acid to hold them in solution.

Iodates of silver, barium, lead, mercury, bismuth, tin, iron, chromium, require more than 500 parts of water at 15° C. to hold them in solution. Iodates of copper, aluminum, cobalt, nickel, manganese, zinc, calcium, strontium, magnesium, sodium, and potassium are more soluble. One hundred ml. of cold water dissolves 0.00385 gram $AgIO_3$ and 0.000035 gram AgI at ordinary temperatures.

Free Iodine (Commercial Crystals).—Iodine is best brought into solution in a concentrated solution of potassium iodide according to the procedure described for standardization of sodium thiosulfate under Volumetric Methods. The iodine is now best determined volumetrically by titration with standard thiosulfate or arsenic.

Iodine or Iodides in Water.—The sample of water is evaporated to about one-fourth its volume and then made strongly alkaline with sodium carbonate. The precipitated calcium and magnesium carbonates are filtered off and washed. The filtrate containing the halogens is evaporated until the salts begin to crystallize out. The hot concentrated solution is poured into three volumes of absolute alcohol and the resulting solution again filtered. The residue is washed four or five times with 95% alcohol. All of the bromine and iodine pass into the solution, whereas a large part of chlorine as sodium chloride remains insoluble and is filtered off. About half a ml. of 50% potassium hydroxide is added and a greater part of the alcohol distilled off with a current of air. The residue is concentrated to crystallization and again poured into three times its volume of absolute alcohol and filtered as above directed. This time only one or two drops of the KOH solution is added and the procedure repeated several times. The final filtrate is freed from alcohol by evaporation, the solution

taken to dryness and gently ignited, then taken up with a little water and filtered. Iodine is determined in the filtrate, preferably by the volumetric procedure III, decomposition with nitrous acid, described under Volumetric Methods.

Organic Substances.—If only an iodide is present, the Carius method is followed; in presence of other halogens, the "lime method" is preferred. Details of these methods are given in the chapter on Chlorine under Preparation and Solution of the Sample.

Silver iodide cannot be separated from the glass of the combustion-tube by solution with ammonium hydroxide as is the chloride or bromide of silver. The compound, together with the glass, is collected upon a filter paper, and washed with dilute nitric acid, followed by alcohol; then dried at 100° C. After removing most of the iodide and the glass, the filter is ignited in a weighed porcelain crucible, the main bulk of the material then added, the substance fused and weighed as AgI+glass. The mass is then covered with dilute sulfuric acid and a piece of pure zinc added. After several hours (preferably over night) the excess zinc is carefully removed and the iodine solution decanted from the glass and metallic silver, and the residue washed by decantation. The silver is now dissolved in hot dilute nitric acid, then filtered from the residue of glass through a small filter. The glass and filter are ignited and weighed. The difference between the two weighings is due to silver iodide.

Minerals. Phosphates.—The substance is decomposed by digestion with (1 : 1) sulfuric acid in a flask through which a current of air passes to sweep out the iodine vapor into a solution of potassium hydroxide, the sample being boiled until all the iodine vapors have been driven into the caustic. Iodates are converted to iodides by reduction with sulfurous acid.

With the iodine content below 0.02%, a 50- to 100-gram sample should be taken.

SEPARATIONS

Separation of Iodine from the Heavy Metals.—The heavy metals are precipitated as carbonates by boiling with solutions of alkali carbonates, the soluble alkali iodide being formed.

Iodine is liberated from combination by nitrous acid.

Silver iodide may be decomposed by warming with metallic zinc and sulfuric acid.

Separation of Iodine from Bromine or from Chlorine.—Details of separation and estimation of the halides in presence of one another are given in the chapter on Chlorine. Advantage is taken of the action of nitrous acid on dilute solutions, free iodine being liberated, while bromides and chlorides are not acted upon.

The solution containing the halogens is placed in a large, round-bottom flask and diluted to about 700 ml. Through a two-holed stopper a glass tube passes to the bottom of the flask; through this tube steam is conducted to assist the volatilization of iodine. A second short tube connected to the absorption apparatus conducts the evolved vapor from the flask into a 5% caustic soda solution containing an equal volume of hydrogen peroxide (about 50 ml. of each). The absorption system may be made by connecting two Erlenmeyer flasks in series,

the inlet tubes dipping below the solutions in the flasks. It is advisable to cool the receivers with ice.

Two to 3 ml. of dilute sulfuric acid (1 : 1) and 25 ml. of 10% sodium nitrite solution are added to the liquid containing the halogens, the apparatus is immediately connected, and the contents of the large flask heated to boiling, conducting steam into it at the same time. The iodine vapor is gradually driven over into the cooled receiving flasks.

When the solution in the large flask has become colorless it is boiled for half an hour longer. The steam is now shut off, the flask disconnected from the receiving flasks and the heat turned off. The contents of the receiving flasks are combined with the washing from the connecting tubes and the solution heated to boiling to expel, completely, hydrogen peroxide. The cooled liquid is acidified with a little sulfuric acid and the solution decolorized with a few drops of sulfurous acid. *Iodine is now precipitated as silver iodide* by adding an excess of silver nitrate and a little nitric acid and boiling the mixture to coagulate the precipitate, which is then dried and weighed.

Chlorine and bromine remain in the large flask in combined form and may be determined in this solution if desired.

Separation of Iodine from Chlorine and Bromine by Precipitation as Palladous Iodide.—The solution containing the halogens is acidified with hydrochloric acid, and palladous chloride solution added to the complete precipitation of the iodide. The compound is allowed to settle in a warm place for twenty-four hours or more and then filtered and washed free of the other halogens. It may now be dried and weighed as palladous iodide, PdI_2, or ignited in a current of hydrogen, then weighed as metallic palladium and the equivalent iodine calculated. See Gravimetric Methods.

GRAVIMETRIC METHODS

PRECIPITATION AS SILVER IODIDE

The procedure is practically the same as that described for determining chlorine.

Silver nitrate solution is added to the iodide solution, slightly acidified with nitric acid. The precipitate is filtered into a weighed Gooch crucible, then washed, dried, gently ignited, and weighed as silver iodide.

$$AgI \times 0.5405 = I \quad \text{or} \quad \times 0.7071 = KI.$$

NOTE.—If filter paper is used in place of a Gooch crucible, the precipitate is removed and the filter ignited separately. A few drops of nitric and hydrochloric acid are added, the acids expelled by heat and the residue weighed as AgCl. This multiplied by 1.638 = AgI. The result is added to the weight of the silver iodide, which is ignited and weighed separately.

DETERMINATION OF IODINE AS PALLADOUS IODIDE

This method is applicable for the direct determination of iodine in iodides in presence of other halogens.

The method of isolation of iodine as the palladous salt has been given under Separations. The salt dried at 100° C. is weighed as PdI_2.

$$PdI_2 \times 0.704 = I.$$

PdI_2 ignited in a current of hydrogen is changed to metallic palladium.

$$Pd \times 2.379 = I.$$

VOLUMETRIC METHODS

DETERMINATION OF HYDRIODIC ACID—SOLUBLE IODIDES

Free hydriodic acid cannot be determined by the usual alkalimetric methods for acids. The procedure for its estimation, free or combined as a soluble salt, depends upon the liberation of iodine and its titration with standard sodium thiosulfate, in neutral or slightly acid solution; or by means of standard arsenious acid, in presence of an excess of sodium bicarbonate in a neutral solution. The following equations represent the reactions that take place:

I. **Thiosulfate.**—$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$

II. **Arsenite.**—$Na_3AsO_3 + I_2 + H_2O = Na_3AsO_4 + 2HI.$

The free acid formed in the second reaction is neutralized and the reversible reaction thus prevented:

$$HI + NaHCO_3 = NaI + H_2O + CO_2.$$

The presence of a free alkali is not permissible, as the hydroxyl ion would react with iodine to form iodide, hypoiodite and finally iodate; hence sodium or potassium carbonates cannot be used. Alkali bicarbonates, however, do not react with iodine.

Standard Solutions. *Tenth Normal Sodium Thiosulfate.*—From the reaction above it is evident that 1 g. molecule of thiosulfate is equivalent to 1 g. atom iodine = 1 g. atom hydrogen; hence a tenth normal solution is equal to one-tenth the molecular weight of the salt per liter, e.g., 24.82 grams $Na_2S_2O_3 \cdot 5H_2O$; generally a slight excess is taken—25 grams of the crystallized salt. It is advisable to make up 5 to 10 liters of the solution by dissolving 125 to 250 grams sodium thiosulfate crystals in hot distilled water, boiled free of carbon dioxide. 0.1 g. of Na_2CO_3 is added per liter of solution. The solution

is allowed to stand a week to ten days, and then standardized against pure, resublimed iodine.

About 0.5 gram of the purified iodine is placed in a weighing bottle containing a known amount of saturated potassium iodide solution (2 to 3 grams of KI free from KIO_3 dissolved in about $\frac{1}{2}$ ml. of H_2O), the increased weight of the bottle, due to the iodine, being noted. The bottle and iodine are placed in a beaker containing about 200 ml. of 1% potassium iodide solution (1 gram KI per 200 ml.), the stopper removed with a glass fork and the iodine titrated with the thiosulfate to be standardized.

Calculation.—The weight of the iodine taken, divided by the ml. thiosulfate required, gives the value of 1 ml. of the reagent; this result divided by 0.012692 gives the normality factor.

NOTE.—The thiosulfate solution may be standardized against iodine, which has been liberated from potassium iodide in presence of hydrochloric acid by a known amount of standard potassium bi-iodate, a salt which may be obtained exceedingly pure.

$$KIO_3 \cdot HIO_3 + 10KI + 11HCl = 11KCl + 6H_2O + 6I_2.$$

A tenth normal solution contains 3.2499 grams of the pure salt per liter. (One ml. of this will liberate 0.012692 gram of iodine from potassium iodide.) The purity of the salt should be established by standardizing against thiosulfate, which has been freshly tested against pure resublimed iodine.

About 5 grams of potassium iodide (free from iodate) are dissolved in the least amount of water that is necessary to effect solution, and 10 ml. of dilute hydrochloric acid (1 : 2) are added, and then 50 ml. of the standard bi-iodate solution. The solution is diluted to about 250 ml. and the liberated iodine titrated with the thiosulfate reagent; 50 ml. will be required if the reagents are exactly tenth normal.

Tenth Normal Arsenite.—From the second reaction above it is evident that As_2O_3 is equivalent to $2I_2$, e.g., to 4H; hence $\frac{1}{4}$ the gram molecular weight of arsenious oxide per liter will give a normal solution: $197.82 \div 4 = 49.455$.

4.95 grams of pure arsenious oxide is dissolved in a little 20% sodium hydroxide solution, the excess of the alkali is neutralized with dilute sulfuric acid, using phenolphthalein indicator, the solution being just decolorized. Five hundred ml. of distilled water containing about 25 grams of sodium bicarbonate are added. If a pink color develops, this is destroyed with a few drops of weak sulfuric acid. The solution is now made to volume, 1000 ml. The reagent is standardized against a measured amount of pure iodine. The oxide may be dissolved directly in sodium bicarbonate solution.

NOTE.—Commercial arsenious oxide is purified by dissolving in hot hydrochloric acid, filtering the hot saturated solution, cooling, decanting off the mother liquor, washing the deposited oxide with water, drying and finally subliming.

Starch Solution.—Five grams of soluble starch are dissolved in cold water, the solution poured into 2 liters of hot water and boiled for a few minutes. The reagent is kept in a glass-stoppered bottle.

The addition of a few mg. of HgI_2, then heating to boiling and filtering will preserve the starch.

DECOMPOSITION OF THE IODIDE BY FERRIC SALTS

The method takes advantage of the following reaction:

$$Fe_2(SO_4)_3+2KI=K_2SO_4+I_2+2FeSO_4.$$

The procedure enables a separation from bromides, as these are not acted upon by ferric salts.

Procedure.—To the iodide in a distillation flask is added an excess of ferric ammonium alum, the solution acidified with sulfuric acid, then heated to boiling, and the iodine distilled into a solution of potassium iodide. The free iodine in the distillate is titrated with standard thiosulfate, or by arsenious acid in presence of an excess of sodium bicarbonate.

The reagent is added from a burette until the titrated solution becomes a pale yellow color. About 5 ml. of starch solution are now added and the titration continued until the blue color of the starch fades and the solution becomes colorless.

One ml. of tenth normal reagent=0.012692 gram iodine, equivalent to 0.012793 gram HI, or 0.016602 gram KI.

DECOMPOSITION WITH POTASSIUM IODATE[3]

The reaction with potassium iodate is as follows:

$$5KI+KIO_3+6HCl=6KCl+3H_2O+3I_2.$$

It is evident that $\frac{5}{6}$ of the titration for iodine would be equal to the iodine of the iodide; hence 1 ml. of tenth normal thiosulfate is equivalent to 0.012692 $\times\frac{5}{6}$=0.01058 gram iodine due to the iodide. The procedure is as follows:

Procedure.—A known amount of tenth normal potassium iodate is added to the iodide solution, in sufficient amount to liberate all of the iodine, combined as iodide, and several ml. in excess. Hydrochloric acid and a piece of calcite are added. The mixture is boiled until all of the liberated iodine has been expelled. To the cooled solution 2 or 3 grams of potassium iodide are added and the liberated iodine, corresponding to the excess of iodate in the solution, is titrated with standard thiosulfate. If 1 ml. of thiosulfate is equal to 1 ml. of the iodate, then the total ml. of the iodate used, minus the ml. thiosulfate required in the titration, gives a difference due to the volume of iodate required to react with the iodide of the sample.

One ml. of N/10 KIO_3=0.01058 gram I in KI.

NOTE.—Tenth normal potassium iodate contains 3.5669 grams KIO_3 per 1000 ml.

DECOMPOSITION OF THE IODIDE WITH NITROUS ACID (FRESENIUS)

Nitrous acid reacts with an iodide as follows:

$$2HNO_2+2HI=2NO+2H_2O+I_2.$$

[3] H. Dietz and B. M. Margosches, Chem. Ztg., 2, 1191, 1904. Treadwell and Hall, "Analytical Chemistry," Vol. 2.

Since neither hydrochloric nor hydrobromic acid is attacked by nitrous acid, the method is applicable to determining iodine in presence of chlorine and bromine; hence is useful for determining small amounts of iodine in mineral waters containing comparatively large amounts of the other halogens.

Nitrous Acid.—The reagent is prepared by passing the gas into conc. sulfuric acid until saturated.

Procedure.—The neutral or slightly alkaline solution of the iodide is placed in a glass-stoppered separatory funnel, Fig. 55, and slightly acidified with dilute sulfuric acid. A little freshly distilled colorless carbon disulfide (or chloroform) is added, then 10 drops of nitrous acid reagent. The mixture is well shaken, the disulfide allowed to settle, drawn off from the supernatant solution and saved for analysis. The liquor in the funnel is again extracted with a fresh portion of disulfide and, if it becomes discolored, it is drawn off and added to the first extract. If the extracted aqueous solution appears yellow, it must be again treated with additional carbon disulfide until all the iodine has been removed (e.g., until additional CS_2 is no longer colored when shaken with the solution). The combined extracts are washed with three or four portions of water, then transferred to the filter and again washed until free from acid. A hole is made in the filter and the disulfide allowed to run into a small beaker and the filter washed down with about 5 ml. of water. Three ml. of 5% sodium bicarbonate are added and the iodine titrated with N/20 or N/50 standard thiosulfate, the reagent being added until the reddish-violet carbon disulfide becomes colorless.

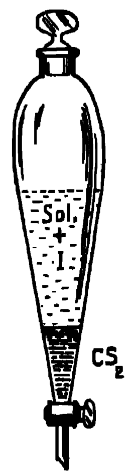


FIG. 55.—Apparatus for Determining Iodine in an Iodide.

The sodium thiosulfate used is standardized against a known amount of pure potassium iodide treated in the manner described above.

One ml. N/20 $Na_2S_2O_3$=.00635 gram I, 1 ml. N/50 $Na_2S_2O_3$=.002538 gram I.

OXIDATION OF IODIDE TO IODINE MONOCHLORIDE[4]

Reaction.—$KIO_3+2KI+6HCl=3ICl+3KCl+3H_2O$. The titration is carried on in a glass-stoppered vessel. The solution of the iodide is treated with an equal volume of conc. HCl and 5 ml. of chloroform are added as an indicating layer. During the titration the chloroform layer is colored with iodine but the color fades sharply with a single drop of 0.1 N(1/60 Molar) KIO_3 at the end-point. The method is selective for iodide in the presence of chloride. A standard solution of potassium permanganate or of ceric sulfate may be used instead of the standard iodate. There are other somewhat similar procedures such as oxidation of iodide to iodine cyanide (Lang's Method), oxidation to iodo-acetone (Berg's method) which can not be discussed in detail here.[5]

[4] L. W. Andrews, Z. anorg. allgem. Chem., 36, 76 (1903); J. Am. Chem. Soc., 25, 756 (1903); G. S. Jamieson, Volumetric Iodate Methods, Chem. Catalog Co., New York, 1926; E. H. Swift and C. H. Gregory, J. Am. Chem. Soc., 52, 894 (1930).

[5] R. Lang, Chap. III, Neuere massanalytische Methoden, F. Enke, Stuttgart, 1937; transl. by Oesper, D. Van Nostrand Co., New York.

DETERMINATION OF IODIDE BY OXIDATION TO IODATE—METHOD OF WINKLER MODIFIED BY KOLTHOFF[6]

Procedure.—Twenty-five ml. of iodide solution (approx. 0.02 N) are treated with 5 ml. of 4 N phosphoric acid, and then a slight excess of freshly prepared 5% bleaching powder solution added until the iodine, that separates, redissolves and the solution becomes colorless. Now 5 ml. of 10% phenol are added and the mixture allowed to stand for 5–10 minutes. Five ml. of N potassium iodide are added and the solution titrated with 0.1 N thiosulfate. One ml. is equivalent to 2.77 mg. KI.

NOTES.—In presence of bromide the solution is treated with 10 ml. of 3% boric acid solution and then with the hypochlorite. The color changes from brown to a darker hue, then brighter and finally pure yellow. Now H_3PO_4, phenol and KI are added followed by immediate titration with thiosulfate, as stated above.

The iodide is oxidized to iodate by the hypochlorite and in presence of bromide liberates free bromine. Chlorine water may be used in place of the bleaching powder solution.

Very dilute iodide solutions may be titrated.

LIBERATION OF IODINE BY MEANS OF HYDROGEN PEROXIDE AND PHOSPHORIC ACID[7]

Principle.—Iodine is liberated from an iodide by addition of hydrogen peroxide to the solution acidified with phosphoric acid, the iodine distilled into potassium iodide and titrated with thiosulfate.

Procedure.—Fifty ml. of the iodide solution are mixed with 5 ml. of pure phosphoric acid and 10 to 20 ml. hydrogen peroxide added, the mixture being placed in a round-bottomed flask, connected with a short condenser, delivering into two absorption vessels containing a 10% solution of potassium iodide. A current of air is drawn through the apparatus, and the contents of the flask gradually heated to boiling. The iodine is absorbed in the potassium iodide solution and titrated as usual with standard sodium thiosulfate. Twenty minutes' heating is generally sufficient.

$$\text{One ml. } Na_2S_2O_3 = 0.012692 \text{ gram I, or } 0.016602 \text{ gram KI.}$$

NOTE.—Iodine in urine may be determined by evaporating to 1/10 its volume. After adding an excess of sodium hydroxide, the mixture is taken to dryness and gently ignited. The ash may be used for the iodine determination.

OXIDATION OF COMBINED IODINE WITH CHLORINE (MOHR'S MODIFICATION OF DUPRÉ'S METHOD)[8]

When a solution of potassium iodide is treated with successive amounts of chlorine water, iodine is liberated, which reacts with an excess of chlorine with formation of chloride of iodine (ICl) and with greater excess the pentachloride (ICl_5), which is changed in presence of water to iodic acid (HIO_3).

Procedure.—The weighed iodide compound is brought into a stoppered flask, and chlorine water delivered from a large burette until all yellow color has

[6] Kolthoff and Furman, Vol. Anal., II. J. Wiley & Sons, Inc., New York, 1929.

[7] E. Winterstein and E. Herzfeld, Z. Physiol. Chem., 63, 49–51, 1909. Chem. Zentralbl., (1), 473–474, 1910.

[8] Sutton, "Volumetric Analysis," 10th Ed.

disappeared. A drop of the mixture brought in contact with a drop of starch solution should produce no blue color. Sodium bicarbonate is now added until the mixture is slightly alkaline, followed by an excess of potassium iodide and 4 to 5 ml. of starch reagent. Standard thiosulfate is now added until the blue color is removed. The excess of chlorine water is thus ascertained. From the value of the chlorine reagent the iodine of the sample may readily be calculated.

The chlorine water is standardized by running 25 to 50 ml. of the reagent into potassium iodide solution (see procedure for bromides, p. 192), and titrating the liberated iodine with standard sodium thiosulfate. The value of the reagent in terms of thiosulfate is thus ascertained and from this the value per ml. in terms of iodine.

OTHER METHODS

VOLHARD'S METHOD FOR DETERMINING IODIDES

This procedure is very similar to those for determining chlorine or bromine, with the exception that silver iodide formed will occlude both the iodide solution and silver nitrate unless the additions of the silver salt are made in small portions with vigorous shaking.

Standard silver nitrate is added to the solution in a glass-stoppered flask, shaking vigorously with each addition. As long as the solution appears milky the precipitation is incomplete. When the silver iodide is coagulated and the supernatant liquid appears colorless, ferric alum solution is added, and the excess of silver nitrate titrated with potassium sulfocyanate until the characteristic reddish end-point is obtained.

The iodine is calculated from the amount of silver nitrate required. E.g., total $AgNO_3$ added, minus excess determined by KCNS = ml. $AgNO_3$ required by the iodine.

NOTE.—The ferric salt oxidizes hydriodic acid with separation of iodine, whereas the silver iodide is not acted upon; hence the indicator is added after all the iodide has combined with silver.

ADSORPTION INDICATOR METHOD (FAJANS)

Iodide ion may be titrated with silver nitrate in solution that is neutral or slightly acidified with $HC_2H_3O_2$, using eosin indicator. The range of application is from 0.1 N down to 0.0005 N halide to be titrated.[9]

[9] Fajans and Wolff, Z. anorg. allgem. Chem., 137, 221, 245 (1924); Kolthoff and van Berk, Z. anal. Chem., 70, 369, 395 (1927).

Procedure.—Iodide alone. From 1–3 drops of 0.5% solution of sodium eosinate in water are added per 10 ml. of 0.1 N halide, or 1–2 drops of indicator per 25 ml. of the more dilute solutions. Titrate with standard silver solution until there is a transition to rose red.

Iodide in presence of chloride. Add 5 ml. of 0.5 N ammonium carbonate per 200–100 ml. of solution, 1–3 drops of eosin indicator, and titrate with standard silver nitrate. In the absence of ammonium carbonate the endpoint appears when more silver has been added than is equivalent to the iodide.

DETERMINATION OF IODATES

The procedure is the reciprocal of the one for determination of iodide by means of an iodate:

Reaction.—$KIO_3+5KI+6HCl=6KCl+3H_2O+3I_2$.

Procedure.—The solution containing the iodate is allowed to run into an excess of potassium iodide solution containing hydrochloric acid. The liberated iodine is titrated with sodium thiosulfate as usual.

One ml. N/10 $Na_2S_2O_3$=0.002934 gram HIO_3, or 0.003567 gram KIO_3.

DETERMINATION OF PERIODATES

The procedure is the same as that described for iodates, the reaction in this case, however, being as follows:

$$KIO_4+7KI+8HCl=8KCl+4H_2O+4I_2.$$

From the equation it is evident that 1 molecule of the periodate is equivalent to 8 atoms of iodine or to 8 atoms of hydrogen; hence $\frac{1}{8}$ the molecular weight per liter of solution would equal a normal solution. Therefore, 1 ml. of a tenth normal solution would contain $0.019193 \div 8 = 0.002399$ gram HIO_4.

One ml. N/10 $Na_2S_2O_3$=0.002399 gram HIO_4, or =0.002849 gram $HIO_4 \cdot 2H_2O$, or =0.002875 gram KIO_4.

DETERMINATION OF IODATES AND PERIODATES IN A MIXTURE OF THE TWO

The procedure depends upon the fact that an iodate does not react with potassium iodide in neutral or slightly alkaline solutions, whereas a periodate undergoes the following reactions:

$$KIO_4+2KI+H_2O=2KOH+KIO_3+I_2.$$

Procedure.—The sample, dissolved in water, is divided into two equal portions.

A. To one portion a drop of phenolphthalein indicator is added and the solution made just faintly alkaline by addition of alkali to acid solution or hydrochloric acid to alkaline solution, as the case may require. Ten ml. of cold saturated solution of sodium bicarbonate are added and an excess of potas-

sium iodide. The liberated iodine is titrated with tenth normal arsenious acid.[10] ($Na_2S_2O_3$ will not do in this case, as the solution is alkaline.)

$$\text{One ml. N/10 } As_2O_3 = 0.0115 \text{ gram } KIO_4.$$

B. To the other portion potassium iodide is added in excess and the solution made distinctly acid. The liberated iodine is titrated with standard sodium thiosulfate. (As_2O_3 will not do.)

Calculation.—In the acid solution, *B*, both iodates and periodates are titrated, whereas in the alkaline solution, *A*, only the periodates are affected. From the reactions for periodates it is evident that 1 ml. $Na_2S_2O_3$ = 4 ml. As_2O_3 for the periodate titration; hence

$$\text{Ml. } Na_2S_2O_3 - \text{ml. } As_2O_3 \times 4 = \text{ml. thiosulfate due to } KIO_3.$$

The difference multiplied by 0.003567 = grams KIO_3 in the sample.

DETERMINATION OF IODINE IN MINERAL WATERS AND BRINES

The following procedure is given by W. F. Baughman and W. W. Skinner.[11]

Take such a quantity of the brine or water as will contain not more than 0.1 g. iodine as iodide or more than 10 g. total salts. Adjust the volume to 100 ml. or 150 ml. and boil it with a sufficient amount of sodium hydroxide and sodium carbonate to precipitate the calcium and magnesium. Filter off the precipitate and wash with hot water. Introduce the filtrate into an Erlenmeyer flask, adjust the volume to about 100 ml., neutralize with dilute sulfuric acid, and add 1 ml. of a solution of sodium hydroxide (4 g. per 100 ml.). Heat to boiling, add an excess of potassium permanganate, continue the heating until the precipitate begins to coagulate, and then allow to cool. Add sufficient alcohol to cause the permanganate color to disappear, and allow the precipitate to settle on the steam bath. Filter and wash with hot water. After cooling, add one or two grams of potassium iodide, acidify with hydrochloric acid, and titrate with standard thiosulfate. The number of ml. required, divided by 6, represents the number of ml. required by the iodine in the sample.

[10] In alkaline solutions the arsenious acid titration must be made, whereas in acid solutions potassium thiosulfate is used.

[11] Bureau of Chemistry, Dept. Agriculture, Washington, D. C. J. Ind. Eng. Chem., 11, 563, 1919.

IODINE, ITS DETERMINATION IN TRACES AS EXISTING IN FEEDSTUFF, WATER, PLANTS, SOILS, TISSUES AND ALLIED MATERIALS [12]

The principal points to be emphasized in the determination of iodine are: (a) Thorough destruction of the organic portion, without loss of iodine; (b) its extraction and measurement, by titration or colorimetrically; (c) the use throughout of reagents iodine free.[13]

Apparatus [14] for the destruction of the carbonaceous material are of the open and closed form, either in acid or alkali medium. The modified closed type suggested by McClendon and Remington [15] because of its simplicity will no doubt be welcomed for certain types of work in iodine determinations. In the estimation of very small quantities ranging from 0.0004 to 0.001 mg. extreme care must be exercised; [16] in such cases one should consult the original papers of von Fellenbergs,[17] R. L. Andrew [18] and Leitch and Henderson.[19]

PREPARATION OF THE SAMPLE

For the determination of iodine in 10.0 ml. of blood see Turner.[12] For the determination of iodine in soils see Andrew.[14] In general samples with estimated amounts of 0.05 mg. or more the following method will suffice. Samples of high water content are dried in oven at 110° C. from 4–5 hours; in rare cases of high fat content, the sample is extracted with ether, though usually not advisable. After dehydration the sample is pulverized. It is now ready to be weighed and treated as follows, which is essentially the modified method of Kendall [20] as suggested by Kelly and Husband.[21]

Place the dried sample of 0.5 to 2.0 g. in a 100-ml. nickel crucible; cover with 40.0% NaOH, heat in oven for one-half hour. Place inside another crucible having sand in the bottom and heat gently over a low flame. When frothing has ceased add about 5 g. of powdered or flaked NaOH. A few milligrams of KNO_3 are added at a time until all carbon is completely oxidized. Cool the melt and extract with boiling water (iodine free). The temperature must be carefully regulated to insure complete oxidation, yet not high enough to volatilize any of the iodine. Transfer the extract to a 700-ml. conical flask (filtering if necessary). The cooled solution is then neutralized with syrupy phosphoric acid, using methyl orange as indicator. Add 2 to 3 ml. in excess of the acid. The solution is boiled for 15–20 minutes to expel any nitrous acid.

[12] Contributed by W. D. Leech.
[13] Reith, J. F., Biochem. Z., 216, 249, 1929.
[14] von J. Schwaibold, Z. anal. Chem., 78, 161, 1929.
[15] Remington et alii, J. Am. Chem. Soc., 52, 3, 1930. McClendon, Remington et alii, J. Am. Chem. Soc., 52, 2, 1930.
[16] Turner, R. G., J. Biol. Chem., 88, 2, 1930.
[17] von Fellenbergs, T., Biochem. Z., 139, 371, 1923, and 152, 116, 1924. von Fellenbergs, Ergeb. Physiol., 25, 176, 1926.
[18] Andrew, R. L., Analyst, 55, 649, 1930.
[19] Leitch and Henderson, Biochem. J., 20, 1003, 1926.
[20] Kendall, J. Biol. Chem. (1920).
[21] Kelly and Husband, Biochem. J., 18, 951, 1924.

Add 2 ml. of 20% sodium acid sulfite and boil for ten minutes to drive off any SO_2. Usually pieces of broken porcelain are added at this point to prevent bumping.

On cooling add 5 to 10 drops of bromine, at least to a distinctly brown color. (Various workers prefer to saturate the solution with chlorine in order to oxidize the iodide to iodate; however, care must be used in the amount added and the duration of boiling to remove the excess. Chlorine is added until a drop of methyl orange is decolorized instantly, followed by two minutes of boiling. Chlorine generated from NaCl, MnO_2 and H_2SO_4 seems to be safe for the above use, but not chlorine from calcium hypochlorite.) Boil at least five minutes after the color of bromine has disappeared to remove the last trace of bromine. Add a few crystals of salicylic acid to liberate any trace of bromine. When the solution is cooled, unglazed porcelain is removed. The KI solution (0.25 g. of recrystallized KI in 20.0 ml. of iodine-free water) is added with 2 ml. of starch solution.[22] The liberated iodine titrated with 0.005 normal thiosulfate (thiosulfate prepared from 0.1 N solution daily; it may be preserved with a crystal of thymol to the 0.1 normal solution). The 0.005 N thiosulfate solution should be standardized each day by setting free the iodine from a standard iodate solution and titrating in the usual way. In this method six times the amount of iodine is titrated as occurs in the unknown sample. According to the following reaction:

$$KIO_3+5KI+3H_2SO_4=3I_2+3H_2O+3K_2SO_4,$$
$$I_2+2Na_2S_2O_3=2NaI+Na_2S_4O_6.$$

The starch solution is prepared by making a paste of 0.5 g. of potato starch, adding to 200 ml. of hot water, boiling for fifteen minutes, stirring continually. Cool, add 0.2 g. of salicylic acid and stir until the crystals dissolve. Iodine-free water is obtained by redistilling distilled water from KOH; KI purified from traces of iodate by recrystallizing from alcohol and finally from iodine-free water, the alcohol being previously distilled over potassium hydroxide.

A control on the reagents should be run, as well as a sample of known iodine content if possible.

[22] Nichols, Ind. Eng. Chem., Anal. Ed. 1, 4, 1929.

IRON [1]

Fe, *at.wt.* 55.84; *sp.gr.* 7.85–7.88; *m.p.* *pure* 1530°, *wrought* 1600°, *white pig* 1075°, *gray pig* 1275°, *steel* 1375°; *b.p.* 2450°; *Ore Oxides* FeO, Fe_2O_3, Fe_3O_4

Next to aluminum, iron is the most common of the metals. It occurs free to a limited extent, sparingly in small grains in certain rocks, in masses in basalt and alloyed in meteorites. It occurs in divalent and trivalent form combined as ferrous and ferric compounds. It is found in a large number of minerals very widely distributed. The more common natural compounds and minerals are—ferrous oxide, FeO; ferric oxide (hematite), Fe_2O_3; magnetite, Fe_3O_4; limonite, $Fe(OH)_3 \cdot Fe_2O_3$; siderite, $FeCO_3$; pyrrhotite, Fe_nS_n; pyrite (Fool's Gold), and marcasite, FeS_2; chalcopyrite, $CuFeS_2$; chromite, $FeO \cdot Cr_2O_3$; göthite, $Fe_2O_3 \cdot H_2O$; almandite, $Fe_3Al_2(SiO_4)_3$; andradite, $Ca_3Fe_2(SiO_4)_3$; ilmenite, $FeTiO_3$; and a large number of combinations with other elements such as manganese, magnesium, zinc, sodium, potassium, nickel, copper, tungsten, lead, arsenic, antimony, etc. The yellow and red color of soils is due principally to iron compounds.

DETECTION

Ferric Iron.—The yellow to red color in rocks, minerals, and soils is generally due to the presence of iron.

Hydrochloric acid solutions of iron as ferric chloride are colored yellow.

Potassium or ammonium thiocyanate produces a red color with solutions containing ferric iron. Nitric acid and chloric acid also produce a red color with potassium or ammonium thiocyanate. This color, however, is destroyed by heat, which is not the case with the iron compound. The red color of ferric iron with the cyanate is destroyed by mercuric chloride and by phosphates, borates, certain organic acids, and their salts, e.g., acetic, oxalic, tartaric, citric, racemic, malic, succinic, etc.

[1] Iron was used during the early history of man in making weapons and tools. It was known to the Assyrians and Egyptians. The production of iron is mentioned in the Pentateuch. High grade steel was manufactured in Arabia and Spain during the Middle Ages. Pure iron finds little commercial use, but with small amounts of other elements it is one of the most important materials used in the industries. The determination of the constituents in ferrous alloys, in pig iron, wrought iron and steel has received a vast amount of attention by chemists and the published analyses predominate with methods dealing with this subject. A special chapter is devoted to steel and ferrous alloys in Volume 2.

Potassium ferrocyanide, $K_4Fe(CN)_6$, produces a deep blue color with ferric salts.

Salicylic acid added to the solution of a ferric salt containing no free mineral acid gives a violet color. Useful for detecting iron in alum and similar products.

Ferrous Iron.—Potassium ferricyanide, $K_3Fe(CN)_6$, gives a blue color with solutions of ferrous salts.

Distinction between Ferrous and Ferric Salts.

KCNS gives red color with Fe''' and no color with Fe''.

$K_3Fe(CN)_6$ gives a blue color with Fe'' and a brown or green with Fe'''.

NH_4OH, NaOH or KOH precipitates red, $Fe(OH)_3$ with Fe''' and white, $Fe(OH)_2$ with Fe'', turning green in presence of air due to oxidation.[2]

Sodium peroxide produces a reddish-brown precipitate of $Fe(OH)_3$ with either ferrous or ferric salt solutions, the former being oxidized to the higher valence by the peroxide. Chromium and aluminum remain in solution, if present in the sample.

ESTIMATION

Iron is so widely diffused in nature that its determination is necessary in practically all complete analyses of ores, rocks, minerals, etc. It is especially important in the evaluation of iron ores for the manufacture of iron and steel.

In the process of analysis iron is obtained in solution as the ferric salt and is precipitated together with aluminum, etc., as the hydroxide by ammonium hydroxide. It is determined most satisfactorily by volumetric procedure, preferably on a separate sample from the aluminum precipitate. If the original valences are desired, one portion is run for total iron and another for ferrous or ferric iron, care being exercised to prevent oxidation or reduction in obtaining the solution.

Iron ores and minerals are brought into solution by treatment with HCl, or HNO_3 or both, or by means of fluxes such as fusion with Na_2CO_3 followed by HCl or by fusion with $KHSO_4$. Ferrous iron is oxidized to ferric form by means of HNO_3 or Br, or Cl or H_2O_2.

PREPARATION AND SOLUTION OF THE SAMPLE

The material should be carefully sampled and quartered down according to the general procedure for sampling. Ores should be ground to pass an 80-mesh sieve. In analysis of metals, both the coarse and fine drillings are taken.

[2] The green salt is a hydrate of Fe_3O_4. The white precipitate can be obtained in absence of air or by using H_2SO_3 to take up oxygen in solution.

The following facts regarding solubility should be remembered: The *element* is soluble in hydrochloric acid and in dilute sulfuric acid, forming ferrous salts with liberation of hydrogen. It is insoluble in concentrated, cold sulfuric acid, but is attacked by the hot acid, forming ferric sulfate with liberation of SO_2. Moderately dilute, hot nitric acid forms ferric nitrate and nitrous oxide; the cold acid gives ferrous nitrate and ammonium nitrate or nitrous oxide or hydrogen. Cold, concentrated nitric acid forms "passive iron," which remains insoluble in the acid. The *oxides of iron* are readily soluble in hydrochloric acid, if not too strongly ignited, but upon strong ignition the higher oxides dissolve with extreme difficulty. They are readily soluble, however, by fusion with acid potassium sulfate followed by an acid extraction. *Silicates* are best dissolved by hot hydrochloric acid containing a few drops of hydrofluoric acid or by fusion with sodium and potassium carbonates, followed by hot hydrochloric acid.

Soluble Iron Salts.—Water solutions are acidified with HCl or H_2SO_4, so as to contain about 3% of free acid.

Ores.—The samples should be pulverized to pass an 80- to 100-mesh sieve.

Sulfides, Ores Containing Organic Matter.—One- to 5-gram samples should be roasted in a porcelain crucible over a Bunsen flame for about half an hour, until oxidized. The oxide is now dissolved as directed in the following procedure.

Oxides, Including Red and Brown Hematites, Magnetic Iron Ore, Spathose Iron Ore, Roasted Pyrites, and Iron Ore Briquettes.—One to 5 grams of the ore, placed in a 400-ml. beaker, is dissolved by adding twenty times its weight of conc. hydrochloric acid with a few drops of 5% stannous chloride solution. Addition of 4 or 5 drops of HF is advantageous if small amounts of silica are present. The solution is covered with a watch-glass and heated to 80 or 90° C. until solution is complete. Addition of more stannous chloride may be necessary, as this greatly assists solution. An excess sufficient to completely decolorize the solution necessitates reoxidation with hydrogen peroxide, hence should be avoided. If a colored residue remains, it should be filtered off, ignited and fused with a mixture of Na_2CO_3 and K_2CO_3 in a platinum crucible. The fusion dissolved in dilute HCl is added to the main filtrate.

NOTE.—The ore placed in a porcelain boat in a red-hot combustion tube may be reduced with hydrogen (taking precaution first to sweep out oxygen with CO_2) and, after cooling in an atmosphere of hydrogen, the reduced iron may be dissolved in acid and titrated.

Iron Silicates.—One to 5 grams of the material, placed in a deep platinum crucible, is treated with ten times its weight of 60% HF and 3 to 4 drops of concentrated H_2SO_4. The mixture is evaporated nearly to dryness on the steam bath and taken up with dilute sulfuric acid or hydrochloric acid. The latter acid is the best solvent for iron.

Fusion with Potassium Bisulfate.—The sample is mixed with ten times its weight of the powdered bisulfate and 2–3 ml. of concentrated sulfuric acid added. A porcelain or silica dish will do for this fusion. The fusion should be made over a moderate flame and cooled as soon as the molten liquid becomes clear. Complete expulsion of SO_3 should be avoided. It may be necessary to cool and add more concentrated sulfuric acid to effect solution. Iron and

alumina completely dissolve, but silica remains undissolved. The melt is best cooled by pouring it on a large platinum lid.

Fusion with Carbonates of Sodium and Potassium.—The residues insoluble in hydrochloric acid are fused with 5 parts by weight of the fusion mixture ($Na_2CO_3+K_2CO_3$) in a platinum crucible. The Méker blast will be necessary. When the effervescence has ceased and the melt has become clear, the crucible is removed from the flame, a platinum wire inserted and the melt cooled. Upon gently reheating, the fuse may be readily removed by the wire in a convenient form for solution in dilute hydrochloric acid.

The bisulfate fusion is recommended for fusion of residues high in iron and alumina. It is an excellent solvent for ignited oxides of these elements. The carbonate fusions are adapted to residues containing silica.

SEPARATIONS

General Procedure.—In the usual course of analysis silica is removed by evaporating the acid solution to dryness, taking up with water and filtering. Mercury, lead, bismuth, copper, cadmium, arsenic, antimony, tin, molybdenum and other elements precipitated from an acid solution as sulfides are removed as such by filtration and iron, after oxidation to the ferric state, is precipitated as $Fe(OH)_3$. In the majority of cases it may now be determined by titration.

Ether Method for Removing Iron from a Solution.[3]—Ferric chloride dissolved in HCl (sp.gr. 1.1) is more soluble in ether than in this acid. Advantage is taken of this fact when it is desired to remove a greater portion of the iron in determining copper, nickel, cobalt, chromium, vanadium and sulfur (as H_2SO_4) in steel. The hydrochloric acid solution of iron, etc., is evaporated to a syrupy consistency and then taken up with HCl (sp.gr. 1.1) and transferred by means of more of the acid to a separatory funnel. The cold acid solution is now extracted several times by shaking with ether, each time allowing the ether carrying the iron to separate before drawing off the lower layer for re-extraction. Three extractions are generally sufficient for removing the iron.

Since alkali salts cause trouble by crystallizing and clogging the borings of the stopcock, the use of alkalies should be avoided when this method of separation is used. The iron may be extracted from the ether by shaking this with water and drawing off the lower water layer. Since heat is generated by the mixing of ether and the ferric chloride-hydrochloric acid solution, cooling the mixture under the tap during mixing may be necessary. This heating is reduced by using a mixture of ether and hydrochloric acid. Conc. hydrochloric acid (sp. gr. 1.19) is saturated with ether, an excess of ether separating out as an upper layer. One hundred ml. of the acid will absorb 150 ml. ether. (Dilute hydrochloric acid (sp.gr. 1.1) absorbs only 30 ml. ether.)

NOTE.—The ether should be free from alcohol.
See also (under Separation) the chapter on Titanium.

The Extraction of Ferric Chloride from Hydrochloric Acid Solutions by Isopropyl Ether.[4]—The efficiency of the extraction with isopropyl ether is very

[3] Noyes, Bray, Spear, J. Am. Chem. Soc., **30**, 515 (1908).
[4] R. W. Dodson, F. J. Forney and E. H. Swift, J. Am. Chem. Soc., **58**, 2573 (1936).

Iron is now precipitated as hydroxide by addition of NH_4OH, the precipitate filtered off and washed with water. The precipitate is again dissolved in HCl and the hydroxide reprecipitated, to remove occluded substances.

Absence of Aluminum and Chromium.—About 1 gram of ammonium chloride salt or its equivalent in solution is added, the volume made to about 200 ml. and ammonium hydroxide added in slight excess to precipitate $Fe(OH)_3$. The solution is boiled for about five minutes, then filtered through an ashless filter.

Second Precipitation.—In either case dissolve the precipitate with the least amount of hot dilute hydrochloric acid and wash the paper free of iron. Add a few ml. of 10% ammonium chloride solution and reprecipitate the hydroxide of iron by adding an excess of ammonium hydroxide, the volume of the solution being about 200 ml. Washing the precipitate by decantation is advisable. Three such washings, 100-ml. portions, followed by two or three on the filter paper, will remove all impurities.

Ignition.—The precipitate is ignited wet over a low flame, gradually increasing the heat. Blasting is not recommended, as the magnetic oxide of iron, Fe_3O_4, will form with high heating. The oxide heated gently appears a reddish-brown. Higher heat gives the black oxide, Fe_3O_4. Twenty minutes' ignition, at red heat, is sufficient.

The crucible, cooled in a desiccator, is weighed and Fe_2O_3 obtained.

Factors. $Fe_2O_3 \times 0.6994 = Fe$.
$Fe_2O_3 \times 0.8998 = FeO$.

NOTE.—**If Aluminum and Chromium are Present.**—In place of ammonium hydroxide powdered sodium peroxide is added in small portions until the precipitate first formed clears, the solution being cold and nearly neutral. It is diluted to about 300 ml. and boiled ten to fifteen minutes to precipitate the iron. Aluminum and chromium are in solution. (Mn will precipitate with Fe, if present.) The precipitate is filtered onto a rapid filter and washed with hot water.

PRECIPITATION OF IRON WITH "CUPFERRON"[5]

By this procedure iron may be precipitated directly in acid solution in presence of a number of elements. Mercury, lead, bismuth, tin, and silver may be partially precipitated. Copper precipitates with iron, but may be easily removed by dissolving it out with ammonia. The method is especially adapted for separation of iron from aluminum, nickel, cobalt, chromium, cadmium, manganese and zinc. Titanium, vanadium and zirconium accompany iron, if present.

Procedure.—The solution containing the iron is made up to 100 ml. and 20 ml. of concentrated hydrochloric acid added. To this cool solution (room temperature) Baudisch's reagent, cupferron, is slowly added with constant stirring, until no further precipitation of iron takes place, and crystals of the reagent appear. The iron precipitate is a reddish-brown. Copper gives a grayish-white flocculent compound. An excess of the reagent equal to one-fifth of the volume of the solution is now added, the precipitate allowed to settle for about fifteen minutes, then poured into a filter paper and washed, first with

[5] O. Baudisch, Chem. Ztg., **33**, 1298, 1905. *Ibid.*, **35**, 913, 1911. O. Baudisch and V. L. King, J. Ind. Eng. Chem., **3**, 627, 1911.

2 N HCl, followed by water, then with ammonia and finally with water. The drained precipitate is slowly ignited in a porcelain or platinum crucible and the residue weighed as Fe_2O_3:

$$Fe_2O_3 \times 0.6994 = Fe.$$

NOTES.—Baudisch's reagent, the ammonium salt of nitrosophenyl-hydroxylamine (cupferron), is made by dissolving 6 grams of the salt in water and diluting to 100 ml. The reagent keeps for a week if protected from the light. It decomposes in the light, forming nitrobenzene. Turbid solutions should be filtered.

The precipitates of copper or iron are but slowly attacked by two normal hydrochloric acid in the cold, but decomposed by hot acid; hence the solution and reagent should be cold.

Cold, dilute potassium carbonate solution, or ammonium hydroxide, has no action on the iron precipitate; the copper compound dissolves readily in ammonia. An alkali hydroxide causes rapid decomposition.

The precipitation is best made in comparatively strong acid solutions (HCl, H_2SO_4, or acetic acid).

VOLUMETRIC DETERMINATION OF IRON IN ORES AND METALLURGICAL PRODUCTS

General Considerations.—Two general procedures are commonly employed in the determination of iron.

A. Oxidation of ferrous to ferric condition by standard oxidizing agents.

B. Reduction of ferric iron to ferrous condition.

The sample is dissolved as directed under Preparation and Solution of the Sample.

DETERMINATION OF IRON BY OXIDATION METHODS

Some modification of either the dichromate or permanganate method is commonly employed in the determination of iron by oxidation. To accomplish this quantitatively, the iron must be reduced to its ferrous condition. This may be accomplished in the following ways:

1. **Reduction by Hydrogen Sulfide.**—During the course of a complete analysis of an ore, H_2S is passed into the acid solution to precipitate the members of that group (Hg, Pb, Bi, Cu, Cd, As, Sb, Sn, Pt, Au, Se, etc.). The filtrate contains iron in the reduced condition suitable for titration with either dichromate or permanganate, the excess of H_2S having been boiled off. If the expulsion of H_2S is conducted in an Erlenmeyer flask there is little chance for reoxidation of the iron during the boiling. Reduction by H_2S is very effective and is frequently advisable. This is the case when titanium is present, since this is not

reduced by H_2S, but by methods given below. Arsenic, antimony, copper, and platinum, which if present, would interfere, are removed by this treatment.

Reaction.—$2FeCl_3+H_2S=2FeCl_2+2HCl+S$.

2. **Reduction with Stannous Chloride.**—$SnCl_2$ solution acts readily in a hydrochloric acid solution of the ore; the reduction of the iron is easily noted by the disappearance of the yellow color. V, Mo and W are also reduced. The excess of the reagent is oxidized to $SnCl_4$ by addition of $HgCl_2$.

Reactions.—1. $2FeCl_3+SnCl_2=2FeCl_2+SnCl_4$.
2. Excess $SnCl_2+2HgCl_2=SnCl_4+2HgCl$ precipitated.

An excess of $SnCl_2$ is advisable, but a large excess is to be avoided, as a secondary reaction would take place, as follows: $2SnCl_2+2HgCl_2=2SnCl_4+2Hg$. This reaction is indicated by the darkening of the solution upon the addition of $HgCl_2$. Precipitation of metallic mercury would vitiate results. The solution should be cooled before addition of mercuric chloride. About 15–20 ml. of saturated mercuric chloride, $HgCl_2$, solution should be sufficient.

3. **Reduction by a Metal such as Test Lead, Zinc, Magnesium, Cadmium, or Aluminum, in Presence of Either Hydrochloric Acid or Sulfuric Acid.**—The former acid is preferred with the dichromate titration, and the latter with the permanganate. Two methods of metallic reduction are in common use—reduction by means of test lead, and reduction with amalgamated zinc by means of the Jones reductor.

(*a*) **Reduction with Test Lead.**—By this method copper is precipitated from solution and small amounts of arsenic and antimony expelled. Sufficient test lead is added to the acid ferric solution to completely cover the bottom of the beaker. The solution is covered and boiled vigorously until the yellow color has completely disappeared, and the solution is colorless. The reduced iron solution, cooled, is decanted into a 600-ml. beaker, the remaining iron washed out from the lead mat by several decantations with water; two or three 50-ml. portions of water should be sufficient; the washings are added to the first portion. If the solution becomes slightly colored, a few drops of stannous chloride, $SnCl_2$, solution are added, followed by 10 ml. mercuric chloride, $HgCl_2$, solution. The sample is now ready for titration.

(*b*) **Reduction with Zinc, Using the Jones Reductor.**—The acid solution of iron, preferably sulfuric acid, is passed through a column of amalgamated zinc.[5] Either the hydrogen evolved or the zinc reduces the ferric iron to ferrous condition. The procedure is described in detail under the Permanganate Method for Determination of Iron, page 474. Titanium, vanadium, chromium, columbium, uranium and tungsten, if present, will also be reduced. The color of the solution will often indicate the presence of contaminants. Molybdenum, chromium and uranium compounds reduced give a green color similar to iron. Columbium and tungsten give a brown color; titanium a violet and vanadium a lavender color. Reduction with zinc is avoided where ferricyanide indicator is used, as zinc salts react with ferricyanide.

[5] Amalgamated zinc is best prepared by dissolving 5 grams of mercury in 25 ml. of concentrated nitric acid with an equal volume of water, 250 ml. of water are added and the solution poured into 500 grams of shot zinc, 20-mesh. When thoroughly amalgamated the solution is poured off, and the zinc dried.

4. Reduction with Sulfurous Acid, Sodium Sulfite or Metabisulfite.—SO_2 gas is passed into a neutral solution of iron, since iron is not reduced readily in an acid solution by this method. The excess SO_2 is expelled by acidifying the solution and boiling. The action is slow.

5. Reduction with Potassium Iodide, the liberated iodine being expelled by heat.

In the solution of the ore with stannous chloride and hydrochloric acid, if an excess of the former has been accidentally added, it will be necessary to oxidize the iron before reduction. This may be accomplished by addition of hydrogen peroxide until the yellow color of ferric chloride appears (or by addition of $KMnO_4$ *solution); the excess* H_2O_2 *may be removed by boiling. The iron may now be reduced by one of the above methods.*

VOLUMETRIC DETERMINATION OF IRON BY OXIDATION WITH POTASSIUM DICHROMATE

Principle.—This method depends upon the quantitative oxidation of ferrous salts in cold acid solution (HCl or H_2SO_4) to ferric condition by potassium dichromate, the following reaction taking place:

$$6FeCl_2+K_2Cr_2O_7+14HCl=6FeCl_3+2CrCl_3+2KCl+7H_2O.$$

Potassium ferricyanide is used as an outside indicator. This reagent produces a blue compound with ferrous salts and a yellowish-brown with ferric. The chromic salt formed by the reaction with iron colors the solution green.

Reagents Required. ***Standard Potassium Dichromate.***—When oxygen reacts with ferrous salts, the following reaction takes place:

$$6FeCl_2+6HCl+3O=6FeCl_3+3H_2O.$$

Comparing this reaction with that of dichromate, it is evident that a normal solution of dichromate contains one-sixth of the molecular weight of $K_2Cr_2O_7$ per liter, namely, 49.037 grams. For general use it is convenient to have two strengths of this solution, N/5 for ores high in iron and N/10 for products containing smaller amounts.

Standardization.—For N/5 solution 9.807 grams of the recrystallized dehydrated salt are dissolved and made up to one liter; N/10 potassium dichromate contains 4.904 grams of the pure salt per liter. It is advisable to allow the solution to stand a few hours before standardization. The Sibley iron ore furnished by the U. S. Bureau of Standards, Washington, D. C., is recommended as the ultimate standard. Other ores uniform in iron may be standardized against the Sibley ore and used as standards.

The equivalent iron in the ore divided by the ml. titration required for complete oxidation gives the value in terms of grams per ml., e.g., 1.4 gram of ore containing 69.2% Fe required a titration of 95 ml. $K_2Cr_2O_7$ solution; then,

$$1 \text{ ml.} = \frac{(69.2\times1.4)}{100} \div 95 = 0.0102 \text{ gram Fe.}$$

Stannous Chloride.—Sixty grams of the crystallized salt dissolved in 600 ml. of conc. HCl and made up to one liter. The solution should be kept well stoppered.

Mercuric Chloride.—Saturated solution of $HgCl_2$ (60 to 100 grams per liter).

Potassium Ferricyanide, $K_3Fe(CN)_6$.—The salt should be free of ferrocyanide, as this produces a blue color with ferric salts, which would destroy the end-point. It is advisable to wash the salt before using. A crystal the size of a pinhead dissolved in 50 ml. of water is sufficient for a series of determinations. The solution should be made up fresh for each set of determinations.

Apparatus. ***Chamber burette.***—This should read from 75 to 90 ml. in tenths and from 90 to 100 ml. in twentieths of a ml.

Test-Plate.—The usual porcelain test-plate with depressions may be replaced by a very simple and efficient test-sheet made by dipping a white sheet of paper in paraffin. The indicator does not cling to this surface, the drops assuming a spherical form, which renders the detection of the end-point more delicate.

Procedure. Iron Ores.—The amount of sample taken should be such that the actual iron present would weigh between 0.9 to 1.1 gram. This weight can be estimated by dividing 95 by the approximate percentage of iron present, e.g., for 50% Fe ore take $\frac{95}{50}=1.9$ gram; 95% iron material would require 1 gram, whereas 20% Fe ore would require 4.75 grams.

For samples containing less than 20% Fe it is advisable to use N/10 $K_2Cr_2O_7$ solution.

The sample should be finely ground (80-mesh).

Solution.—The hydrochloric acid method for solution of the oxidized ore with subsequent carbonate fusion of the residue is recommended as being suitable for iron ores, briquettes, and materials high in iron.

Reduction by Test Lead.—The easy manipulation and efficiency of this method of reduction make it applicable for a large variety of conditions. The acid solution, preferably HCl, is diluted to about 150 to 200 ml., containing 15 to 20 ml. concentrated hydrochloric acid (sp.gr. 1.19). Sufficient test lead is added to cover the bottom of a No. 4 beaker. The solution covered is boiled vigorously until it becomes colorless. Copper, if present, is precipitated as metallic copper, and small amounts of arsenic and antimony eliminated from the solution during the reduction of the iron. The cooled solution is poured into a 600-ml. beaker and the mat of lead remaining in the No. 4 beaker washed free of iron, two or three 50-ml. washings being sufficient. The main solution and washings are combined for titration. If the solution is slightly colored, due to reoxidation of iron, a few drops of stannous chloride solution are added to reduce it, followed by an excess of $HgCl_2$ solution, 20 to 25 ml., and allowed to stand five minutes.

Titration.—The standard potassium dichromate is run into the solution to within 5 to 10 ml. of the end-point, this having been ascertained on a portion of the sample. The dichromate is run in slowly near the end-reaction, and finally drop by drop until a drop of the solution mixed with a drop of potassium ferricyanide solution produces no blue color during thirty seconds. A paraffined surface is excellent for this test.

Ml. $K_2Cr_2O_7$ multiplied by value per ml. = Fe present in sample. %
$= \frac{Fe \times 100}{\text{wt. taken}}$.

NOTES.—If $SnCl_2$ solution has been used for reduction of the iron, it is necessary to add the $HgCl_2$ rapidly to a cold solution, as slow addition to a warm solution is apt to precipitate metallic mercury.

In case an excess of dichromate has been added in the titration, as often occurs, back titration may be made with ferrous ammonium sulfate, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$. N/10 solution of this reagent may be prepared by dissolving 9.81 grams of the clear crystals in about 100 ml. of water, adding 5 ml. of concentrated H_2SO_4 and making to 250 ml. The solution should be standardized against the dichromate solution to get the equivalent values, by running the dichromate directly into the ferrous solution.

The ferricyanide indicator should be made up fresh each time it is required.

Large amounts of manganese in the iron solution titrated cause a brown coloration, which masks the end-point. Nickel and cobalt, present in large amounts, are objectionable for the same reason. This interference may be overcome by using very dilute acid solutions of ferricyanide indicator, so that the insoluble ferricyanide of these metals will not form.

If ferricyanide indicator is used reduction of iron by zinc cannot be done, as zinc compounds react with ferricyanide. The blue color develops slowly. Allow 3 minutes, if necessary.

DICHROMATE METHOD FOR IRON WITH DIPHENYLAMINE INDICATOR

The disadvantage of the dichromate method in requiring an outside indicator (potassium ferricyanide on a spot plate) is overcome by the procedure outlined by J. Knop (J. Am. Chem. Soc., **46**, 263, 1924) in which diphenylamine is used as an internal indicator, the end-point being a violet-blue or blue-black.

Reagents.—***0.1 N Potassium Dichromate*** solution.

Sulfuric-Phosphoric Acid Mixture.—150 ml. sulfuric acid (sp.gr. 1.84), 150 ml. phosphoric acid (d. 1.7), diluted to 1000 ml., 15 ml. used.

Diphenylamine solution. One g. diphenylamine dissolved in 100 ml. of conc. sulfuric acid. Three drops used as indicator. (A color change to brown does not impair the efficiency of the indicator.)

Procedure for Ores.—Half to 1 gram of the ore is digested with 20 ml. of conc. hydrochloric acid at 70–80° C., the solution diluted with an equal volume of water and filtered. The insoluble residue is fused with sodium carbonate in a platinum crucible, the melt dissolved in dilute hydrochloric acid, the iron precipitated with ammonium hydroxide and filtered off. The ferric hydroxide on the filter is dissolved with a few ml. of dilute HCl and the solution added to the main solution containing the iron.

The iron is now reduced by addition of stannous chloride solution (60 g. $SnCl_2$ in 600 ml. HCl and 400 ml. H_2O) added cautiously until the color of iron is no longer evident (other reducible elements must be absent, i.e., Cu, As, etc.); the excess of stannous chloride is overcome with mercuric chloride solution (saturated solution) as usual.

Fifteen ml. of sulfuric-phosphoric acid mixture are added and 3 drops of diphenylamine indicator, the solution is diluted to 150–200 ml. and titrated with 0.1 N potassium dichromate solution.

Near the end the green color of the solution deepens to a blue-green or in presence of a large amount of iron to a grayish blue. The dichromate is now added dropwise until the color changes to an intense violet blue.

$$1 \text{ ml. } 0.1 \text{ N } K_2Cr_2O_7 = 0.0056 \text{ g. Fe.}$$

NOTES.—The method has the advantage of having no fading end-point as is obtained in the permanganate titrations in presence of mercurous chloride. The method permits back titration with standard ferrous solution. Organic substances do not interfere as they do in permanganate titrations. Zinc, aluminum, manganese, nickel, cobalt and chromium do not interfere. Copper present in quantities less than 1 mg. does not interfere; in larger quantities it lowers results as it assists oxidation of iron by air. Trivalent arsenic raises results as it is oxidized by dichromate to pentavalent form.

"Determination of Iron with Potassium Dichromate." L. Szebellédy, Z. anal. Chem., 81, 97–103, 1930.—"*p*-Phenetidine can be used in place of diphenylamine as inside indicator in the titration of Fe^{++} with $K_2Cr_2O_7$. The solution assumes a violet-red color as soon as an excess of dichromate has been added. To remove $FeCl_3$, NH_4F can be used to advantage in place of H_3PO_4. To 50 ml. of Fe solution in a 100-ml. Jena flask add 10 ml. of 9 N H_2SO_4 and 1 ml. of 1% *p*-phenetidine solution. To remove dissolved air, add 2 g. of $KHCO_3$ in several portions and with the last portion add 3 g. of NH_4F. Add the $K_2Cr_2O_7$ solution until a permanent reddish-violet color is obtained. Numerous experiments are described with this indicator." C. A., 24, 4729, 1930.

L. A. Sarver recommends keeping the volume below 100 ml. (J. Am. Chem. Soc., 49, 1473, 1927).

CERIC SULFATE TITRATION METHOD

Standard ceric sulfate solution (see Chapter on Standard Solutions) is one of the most satisfactory reagents for the titration of ferrous iron, especially in solutions containing hydrochloric acid; sulfuric, perchloric nitric and acetic acids do not interfere with titrations by ceric sulfate; hydrofluoric and phosphoric acids may be present in fairly high concentrations. The iron is reduced by any conventional method, after which 2 drops of 0.025 M o-phenanthroline indicator, or 5 drops of 0.1% aqueous solution of erioglaucine or eriogreen is added as indicator. o-Phenanthroline ferrous sulfate is the most satisfactory indicator for general use: Change deep red to pale blue at the end of oxidation of ferrous iron. Erioglaucine (or eriogreen) is especially suitable for indication when the iron has been reduced by the stannous chloride-mercuric chloride method. The presence of calomel does not interfere with the action of the indicator, which changes to pale rose when all of the iron has been oxidized.[7]

POTASSIUM PERMANGANATE METHOD FOR DETERMINATION OF IRON

Introduction.—The method depends upon the quantitative oxidation of ferrous salts to the ferric condition when potassium permanganate is added to their cold solution, the following reaction taking place:

$$10FeSO_4+2KMnO_4+8H_2SO_4=5Fe_2(SO_4)_3+K_2SO_4+2MnSO_4+8H_2O.$$

Hydrochloric acid in presence of iron salts has a secondary reaction upon the permanganate, e.g.,

$$2KMnO_4+16HCl=2KCl+2MnCl_2+8H_2O+10Cl.$$

This reaction may be prevented by addition of large amounts of zinc or manganous sulfates together with an excess of phosphoric acid or by large dilu-

[7] Willard and Young, J. Am. Chem. Soc., 50, 1334 (1928); 55, 3260 (1933); Furman and Wallace, 52, 2347 (1930).

tion. See note on page 476. The solution is diluted and reduced with zinc and titrated as directed.

The reduction of ferric sulfate is best accomplished by passing the solution through a column of amalgamated zinc in the Jones reductor. In presence of titanium, vanadium, chromium, uranium, and arsenic reduction is accomplished by H_2S in a hydrochloric acid solution of the iron, or by SO_2 or $SnCl_2$.

Since potassium permanganate enters into reaction with acid solutions of antimony, tin, platinum, copper and mercury, when present in their lower state of oxidation (also with manganese in neutral solutions), and with SO_2, H_2S, N_2O, ferrocyanides and with most soluble organic bodies, these must be absent from the iron solution titrated.

Potassium permanganate produces an intense pink color in solution, so that it acts as its own indicator.

Solutions Required. *Standard Permanganate Solutions.*—As in the case of potassium dichromate, it is convenient to have two standard solutions, N/5 and N/10.

From the reaction given above it is evident that $2KMnO_4$ are equivalent to 5 oxygens, e.g., $2KMnO_4 = K_2O + 2MnO + 5O$; hence a normal solution would contain one-fifth of the molecular weight of $KMnO_4 = 31.6$ grams of the pure salt.

Since commercial potassium permanganate is seldom pure, it is necessary to determine its exact value by standardization. This is commonly accomplished by any of the following methods:

(*a*) By a standard electrolytic iron solution.
(*b*) By ferrous salt solution, e.g., $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$.
(*c*) By oxalic acid or an oxalate.

Reaction.—$2KMnO_4 + 5Na_2C_2O_4 + 8H_2SO_4$
$$= K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 10CO_2 + 8H_2O.$$

Standardization of $KMnO_4$ against *sodium oxalate* is recommended as the most accurate procedure.

To standardize.—0.2 g. of pure sodium oxalate, equivalent to 0.2 ÷ .0067 = 29.9 ml. 0.1 N solution (or if preferred 0.67 g. = 100 ml. 0.1 N solution), is dissolved in 100 ml. hot water and 5–10 ml. H_2SO_4 (sp.gr. 1.84) and titrated with the permanganate solution until a faint pink color, that persists, is obtained. The oxalate equivalent in ml. divided by ml. $KMnO_4$ required = normality of $KMnO_4$, in terms of N/10 solution.

PROCEDURE FOR THE DETERMINATION OF IRON BY THE JONES REDUCTOR

Preparation of Sample.—Such an *amount* of the sample is taken that the iron content is between two- and three-tenths of a gram (0.2 to 0.3 gram). If hydrochloric acid has been required to effect solution, or hydrochloric acid and nitric acid (25 : 1), as in case of iron and steel, 4 to 5 ml. concentrated sulfuric are added, and the solution evaporated to small bulk on the steam bath

and to SO_3 fumes to remove hydrochloric acid. The iron is taken up with about 50 ml. dilute sulfuric acid, (1 : 4), heating if necessary, and filtering if an insoluble residue remains.[8]

Preparation of the Reductor.—Cleaning out the apparatus. See Fig. 56. The stop-cock of the reductor is closed, a heavy-walled flask or bottle is put into position at the bottom, and 50 ml. of dilute sulfuric acid poured into the funnel. The cock is opened and the acid allowed to flow slowly through the zinc in the tube, applying a gentle suction. Before the acid has drained out of the funnel, 50 ml. of water are added, followed by 50 ml. more of dilute sulfuric acid and 50 ml. of water in turn. The stop-cock is turned off before the water has drained completely from the funnel so that the zinc is always covered by a solution of acid or water.

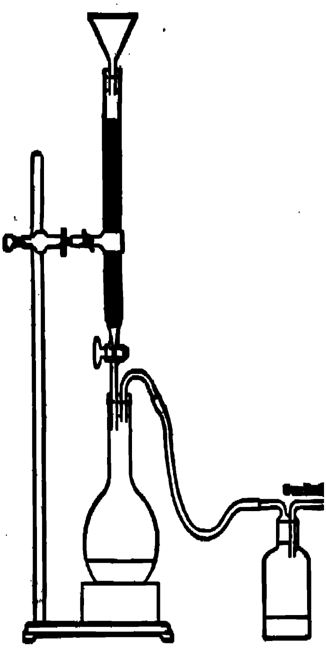


FIG. 56.—Jones Reductor.

Determination of the Blank.—Fifty ml. of dilute sulfuric acid, (1 : 4), are passed through the reductor, followed by 250 ml. of distilled water, according to the directions given above. The acid solution in the flask is then titrated with N/10 $KMnO_4$ solution. If more than 3 or 4 drops of the permanganate are required, the operation must be repeated until the blank titration does not exceed this amount. The final blank obtained should be deducted from the regular determinations for iron. The end-point of the titration is a faint pink, persisting for one minute.

Reduction and Titration of the Iron Solution.—The sample is diluted to 200 ml., and, when cold, is run into the funnel, the stop-cock opened and the solution drawn slowly through the column of zinc into the flask, about four minutes being required for 200 ml. of solution. Before the funnel has completely drained, rinsings of the vessel which contained the sample are added; two 50-ml. portions are sufficient, followed by about 50 ml. of water. The stop-cock is closed before the solutions have completely drained from the funnel.

Titration.—The flask is removed and tenth normal solution of permanganate added until a faint pink color, persisting one minute, is obtained. The blank is deducted from the ml. reading of the burette.

One ml. N/10 $KMnO_4$=.005584 gram Fe; or .007984 gram Fe_2O_3.

[8] The titration may be conducted in presence of HCl by adding $MnSO_4$ and H_3PO_4. "Zimmermann-Reinhardt reagent," or by high dilution. (Reagent—200 g. $MnSO_4 \cdot 4H_2O$ + 100 ml. H_2O + 400 ml. syrupy H_3PO_4.)

OPTIONAL PERMANGANATE METHOD FOR IRON IN ORES

1. **Solution of the Sample.**—0.5 gram of ore. 8-oz. flask. With oxidized ores add 10–15 ml. of HCl and warm gently until the iron oxide is dissolved; then if sulfides are also present add 5 ml. of HNO_3 to decompose them also. With straight sulfides use 10 ml. of HCl and 5 ml. of HNO_3. When decomposition is complete add 5 ml. of H_2SO_4 and boil over a free flame nearly to dryness.

Refractory Ores.—Certain silicates, oxides of iron, furnace slags, etc., do not decompose with acid treatment. Decomposition may be accomplished by fusion methods followed by solution of the fused mass with water and hydrochloric acid. Fusions with Na_2CO_3 and K_2CO_3 are made in a nickel or platinum crucible and are recommended for materials high in silica. Fusions with an acid flux, K_2SO_4 (+5 ml. H_2SO_4 sp.gr. 1.84) or $KHSO_4$ are recommended for oxides. These latter fusions are conveniently carried out in Pyrex flasks held by a heavy wire clamp. About 10–15 grams of the solid flux is added to the ore in the flask and the fusion completed by heating until the mix becomes transparent. Oxides which do not readily decompose may be brought into solution, frequently, by adding a little piece of filter paper to the molten mass in the flask. The carbon thus furnished reduces the oxides, effecting decomposition. If decomposition is incomplete, the water and acid extraction is made, the soluble constituents decanted off and the residue again fused with more $KHSO_4$ and filter paper. It may be necessary to follow $KHSO_4$ fusion by the Na_2CO_3 fusion, on the insoluble residue remaining from the acid extraction of the $KHSO_4$ mass.

2. **Reduction.**—After cooling, add 30 ml. water, 10 ml. HCl and 6 grams of 20-mesh granulated zinc. It is not necessary to get salts into solution. Now add 3 ml. of a 4% copper sulfate solution. Allow to stand until the action has become feeble.

3. Add 50 ml. of cold water and then 10 ml. of conc. H_2SO_4 and allow to stand until the zinc is nearly all dissolved.

4. **Filtration from Insoluble Gangue and Excess Zinc.**—Prepare a filter by placing a rather thick wad of absorbent cotton in a funnel and wetting it into place. Place a battery jar, or a liter beaker containing about an inch of cold water, under the funnel. Have the beaker marked at the 700-ml. point.

5. When the zinc in the flask has nearly all dissolved, filter the liquid through the absorbent cotton and wash out the flask at least 10 times with cold water, pouring through the filter. Use the wash bottle reversed to save time, and use enough water for each wash to completely cover the absorbent cotton. Allow to drain between washes. Continue the washing until the filtrate reaches the 700-ml. mark on the beaker.

6. **Titration of the Sample.**—Titrate at once with standard permanganate to a very faint pink tinge and take reading.

7. A blank should previously be run on the zinc to determine any correction (usually due to a little iron) necessary. Deduct this correction from the above reading.

8. Multiply the ml. of permanganate used by the factor for iron.

Diphenylamine Indicator in Permanganate Titrations of Iron.[1]—As in case of titrations of iron with potassium dichromate, diphenylamine may be used in potassium permanganate titrations. The advantage of the indicator is in the fact that titrations may be made in presence of considerable hydrochloric acid and in the presence of tin and mercury salts without a fading end-point, obtained when permanganate is used alone. The blue color is more intense than the pink of potassium permanganate.

Procedure. *Decomposition and Reduction of Sample.*—The procedure given on page 474 applies also to this method.

Titration.—About 15 ml. of phosphoric-sulfuric acid mixture are added and the solution is diluted to about 100 ml. 0.2 ml. (4 drops) of diphenylamine indicator is added and the titration now made with the standard potassium permanganate solution. The color becomes green, deepening to a blue-green or grayish blue. The reagent is now added "dropwise" until an intense violet blue or dark blue color is obtained.

$$1 \text{ ml. } 0.1 \text{ N } KMnO_4 = 0.005584 \text{ g. Fe.}$$

NOTES.—If 0.5584 gram of sample is taken, then 1 ml. of 0.1 N potassium permanganate is equivalent to 1% of iron.

The phosphoric-sulfuric acid mixture prevents the yellow color of iron from producing a green with the blue end-point. A larger amount of indicator than is recommended should not be used, as this necessitates a blank being deducted for the action of the oxidizing agent on the indicator.

Standardization of Potassium Permanganate-Oxalate Method.—Weigh 0.2 to 0.3 gram of pure sodium oxalate, place in a beaker and add 200 ml. of water and about 5 ml. conc. sulfuric acid. Heat to boiling and titrate with the potassium permanganate solution. The reaction starts slowly, but with the progress of the titration the action becomes vigorous. Towards the end of the reaction the pink color fades less rapidly and finally a permanent pink color is obtained with one drop of the reagent.

Calculation of Normality.—Since 67 grams of sodium oxalate per 1000 ml. of solution is a normal solution, the ml. equivalent of the amount taken is obtained by dividing by 0.067. This value divided by the titration of the oxalate with the reagent being standardized will give the normality of the reagent.

Example.—Suppose 0.268 gram of sodium oxalate required a titration of 50 ml. of the permanganate solution. Since 67 g. is equivalent to 1000 ml. N solution of sodium oxalate, then 0.268 is equivalent to

$$0.268 \times 1000 \text{ divided by } 67 = 4 \text{ ml. N soln.}$$
$$4 \text{ divided by } 50 = 0.08 \text{ N.}$$

[1] Wilfred W. Scott, J. Am. Chem. Soc., 46, 1396, 1924.

DETERMINATION OF FERRIC IRON BY TITRATION WITH A TITANOUS SALT SOLUTION

METHOD OF KNECHT AND HIBBERT [10] (MODIFIED BY THORNTON, CHAPMAN, AND WOOD [11])

Introduction.—The iron solution, which may contain hydrochloric acid, sulfuric acid, or hydrofluoric acid (provided boric acid be added in considerable excess), but not nitric acid, is titrated while cold (about 20° C.) with a standard solution of titanous sulfate,[12] using potassium thiocyanate as indicator, until the red color of the ferric thiocyanate just disappears.

Any substance that might reduce the ferric iron or oxidize the titanous salt should, of course, be absent. Many forms of organic matter, however, do not interfere. Copper is quantitatively precipitated as cuprous thiocyanate, and certain other metals of the hydrogen sulfide group are not without effect. Platinum salts, chromic acid (but not chromic salts), and vanadic acid exert an oxidizing action on the titanium compound.

Reagents. *Titanous Sulfate Solution (1/10 Normal).*—The titanium solution is prepared by mixing 100 ml. of a 20% solution of titanous sulfate with 80 ml. of sulfuric acid (1 : 1) and making the volume up to 1 liter with cold water.

Potassium Thiocyanate Solution.—One hundred grams of the crystals are dissolved in water, the resulting solution is filtered, and the clear filtrate is diluted to 1 liter.

Ferric Ammonium Sulfate Solution.[13]—Forty-eight grams of ferric alum crystals are dissolved in water, the solution is acidified with 50 ml. of concentrated sulfuric acid, and the volume is made up to 1 liter.

Apparatus.—The titanous sulfate solution, prepared as described above, is charged into the storage bottle *S*, Fig. 57, the volume being so regulated as to fill the container to its neck. The stop-cock *E* is then turned so that the liquid rises in the burette *B* and continues upwards until hydrostatic equilibrium has been attained. With the hydrogen supply from the Kipp generator *K* turned on, the burette is allowed to empty itself by properly manipulating the cock *F*,

[10] E. Knecht and E. Hibbert, "New Reduction Methods in Volumetric Analysis," pp. 10 and 68, 1925. Longmans, Green and Co.

[11] W. M. Thornton, Jr., and J. E. Chapman, J. Am. Chem. Soc., 43, 91, 1921; W. M. Thornton, Jr., and A. E. Wood, J. Ind. Eng. Chem., 19, 150, 1927.

[12] E. Knecht and E. Hibbert employ titanous chloride, which for most purposes is equally satisfactory. A high-grade titanium trichloride (15% solution) may be purchased from Schering-Kahlbaum, A. G. (Akatos, Inc., 114–118 Liberty St., New York City). See I. M. Kolthoff and O. Tomiček, Rec. trav. chim., 43, 776, 1924. A N/10 solution of titanous sulfate can be prepared in the following manner: Thirty-eight grams of potassium titanium oxalate ($K_2TiO(C_2O_4)_2 \cdot 2H_2O$), 32 grams of ammonium sulfate, and 80 ml. of concentrated sulfuric acid are placed in a 750-ml. Kjeldahl flask and heat is applied very carefully till frothing has ceased; thereafter the solution is boiled to decompose the oxalate. After cooling and diluting to 1000 ml., the solution is filtered, and the titanium is reduced by passing the liquid slowly through a Jones reductor, the latter having a bore of 2 cm. and containing a column of amalgamated zinc 45 cm. long. The deoxidized solution is mixed by bubbling carbon dioxide through it just prior to being poured into the storage bottle. Cf. W. M. Thornton, Jr., and R. Roseman, Am. J. Sci. (5), 20, 14, 1930.

[13] The ferric alum solution will serve for a "back titration" in any analysis, and it will enable the operator to quickly detect any change in the oxygen-consuming capacity of the titanous salt solution.

and a current of hydrogen is maintained through the apparatus till it is reasonably certain that all air has been displaced from within the system. It suffices to pass a slow stream of the protecting gas for about an hour; though it may be well also, after letting the solution stand for a day or two, to repeat the sweeping for a shorter interval (say fifteen minutes). After each attempt to

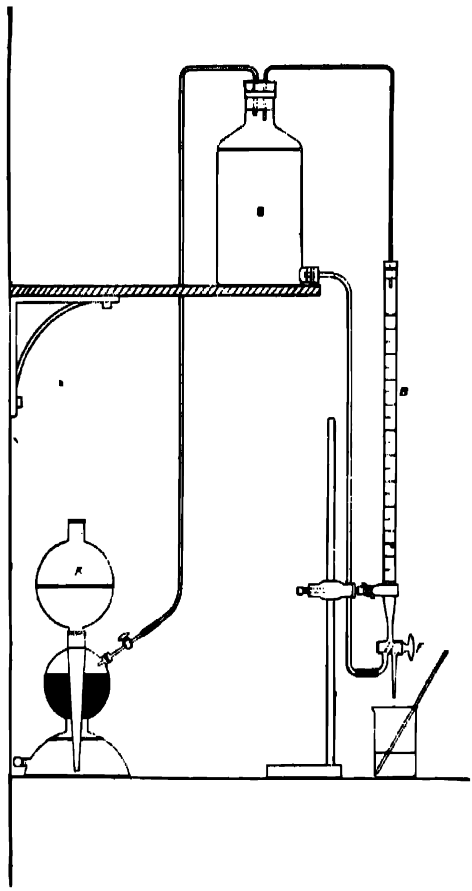


FIG. 57.—Apparatus for Storing and Using a Titanous Salt Solution.
J, Rubber-tubing connection; *T*, thermometer with enclosed scale; *G*, glass-wool filter.

remove the air, the burette is refilled, in which state it is ready for service. The rubber connections should be wired and coated with shellac varnish. If the apparatus is carefully assembled, the standard reagent will show a change of titer considerably less than one part in a thousand per month; certainly, as far as the solution in the bottle is concerned.

Standardization.—Some specimens of ferrous ammonium sulfate, as procured in the market, contain very nearly the theoretical amount of iron (14.24%), this being the total quantity of iron and not simply that present in the ferrous condition; but it is hardly safe to make this assumption with

samples of the salt that have not been tested.[14] On the other hand, the "Sibley" iron ore,[15] which may be obtained from the Bureau of Standards with certified analysis, is a reliable standard.

Against Ferrous Ammonium Sulfate.—One and five-tenths grams of the C. P. crystals are weighed into a 300-ml. Erlenmeyer flask and dissolved in 90 ml. of water. Ten ml. of sulfuric acid (1 : 1) are added, and the solution is titrated with N/10 potassium permanganate, which, by the way, need not have been standardized until the end-point is reached. *After boiling for ten minutes,*[16] *the liquid is permitted to cool thoroughly,* 5 ml. of the thiocyanate solution are introduced, and the flask is joined to the burette in the manner shown in the cut (Fig. 57). The air is expelled from within the reaction vessel by passing a moderately rapid current of carbon dioxide through the test solution for five minutes; whereupon, while continuing the flow of carbon dioxide, the titanous sulfate is added dropwise till there is no further diminution of color, allowing ample time, when nearing the end of the titration, for each portion to exert its full effect before introducing the next.

Against the "Sibley" Iron Ore.—About 1.5 grams of the ore (previously dried at 100° C.) are weighed with exactness and dissolved in 10 ml. of concentrated hydrochloric acid, using for the dissolution a small Erlenmeyer flask fitted with a cut-off calcium chloride tube to serve as a trap,[17] and adding about 3 drops of hydrofluoric acid toward the end to decompose the silica (and silicates). This solution is transferred to a Pyrex evaporating basin, 25 ml. of sulfuric acid (1 : 1) are added, and the hydrochloric and hydrofluoric acids are removed—as completely as may be—by evaporating on the steam-bath. The residue is taken up with water, heating if necessary, the solution cooled, transferred to a 500-ml. volumetric flask; and, the volume being about 300 ml., it is oxidized with permanganate as described above, omitting, however, the subsequent boiling. The solution is then diluted to the mark and aliquot portions of 100 ml. each are taken with an accurate pipette. The remaining procedure is the same as that given under *Ferrous Ammonium Sulfate.*

Procedure. ***Ferric Iron.***—The solution, which may contain any amount of iron up to 0.28 gram,[18] and which should preferably occupy a small volume (not much greater than 100 ml.), is titrated with titanous sulfate—using the same quantities of reagents and in other respects proceeding as prescribed above.

Total Iron.—To determine the entire amount of iron in a given material, notwithstanding its state of oxidation, the whole of it must be gotten into the ferric condition. This may be accomplished in any one of three ways: (1) the solution is treated with ammonia and hydrogen peroxide and boiled to decompose the excess of peroxide and finally acidified with hydrochloric acid; (2) the

[14] W. M. Thornton, Jr., and A. E. Wood, *loc. cit.*, p. 153.

[15] Bur. Standards, Standard Sample No. 27a. Cf. T. F. Buehrer and O. E. Schupp, Jr., J. Ind. Eng. Chem., 18, 121, 1926.

[16] The boiling serves to destroy the small excess of permanganate. An alternate procedure is to add 5 to 10 ml. of an approximately N/10 solution of sodium arsenite to the test solution, which should also contain hydrochloric acid (P. S. Brallier, J. Ind. Eng. Chem., 19, 846, 1927).

[17] F. A. Gooch and P. E. Browning, Am. J. Sci. (3), 39, 197, 1890.

[18] On the determination of very small amounts of iron by means of titanous sulfate see J. F. King and R. N. Washburne, J. Phys. Chem., 30, 1688, 1926.

sulfuric acid solution is titrated with permanganate until the pink color just becomes visible (see standardization); (3) the ferrous salt is oxidized with potassium chlorate in the presence of hydrochloric acid and the excess of the chlorate is removed by evaporation. The second method is generally to be preferred. Large amounts of hydrochloric acid may be expelled by evaporating on the steam-bath with sulfuric acid in excess; but with small concentrations of said acid the evil effect upon permanganate may be offset by adding a sufficient quantity of the Zimmermann-Reinhardt preventive reagent, leaving out, of course, the phosphoric acid.[19] This is prepared by dissolving 67 grams of manganous sulfate ($MnSO_4 \cdot 4H_2O$) in 500 ml. of water, adding 130 ml. of sulfuric acid (sp.gr. 1.82), and diluting to 1000 ml.

IODOMETRIC DETERMINATION OF IRON

Iron in the ferric form may be determined iodometrically, as in case of cupric ion determination. The reaction of the iodide ion with iron is:

$$2Fe^{+++} + 2I^- = 2Fe^{++} + I_2^\circ.$$

Procedure.—The solution, free from other substances liberating iodine from KI and containing about 2 ml. of 4 N HCl per 10 ml., is treated with about 1–2 g. KI and titrated with standard solution of thiosulfate as in case of the copper determination, using starch as an indicator.

One ml. 0.1 N thiosulfate is equivalent to 0.005584 g. Fe.

THIOSULFATE TITRATIONS OF SMALL AMOUNTS OF IRON IN GLASS SANDS[20]

Apparatus and Reagents.—*Silver Dishes*, 4" diam. by 2" deep, 999.5–999.75 fine-

Potassium Iodide Solution.—120 g. KI in 200 cc.

Starch Solution.—500 ml. clear cold common salt (NaCl) solution mixed with 100 ml. glacial acetic acid and 3 g. soluble starch. Bring just to a boil and then cool for use.

Standard Thiosulfate Solution.—1.55 g. $Na_2S_2O_3 \cdot 5H_2O$ crystals in solution boiled one hour and diluted to one liter with freshly boiled water. Sterilize container and measuring flask and burette by rinsing first with conc. HCl and then with boiled water.

To Standardize.—Weigh 15–16 mg. iron wire (2" of No. 30 gauge) on a gold button balance, or precisely 10 inches on an analytical scale, and divide the latter into five equal lengths.

Dissolve each portion in 150-ml. beaker by mixture of 3 ml. water and 1 ml. HNO_3, boil out nitrous fumes, add a crystal of chlorate to oxidize carbonaceous matter, heat a moment, dilute to 100 ml., add ammonia in excess, boil, filter on 9 cm. paper, wash, discard filtrate, wash the ferric hydroxide from the paper into a 180-ml. "copper" flask by means of a wash bottle jet, place the flask beneath the funnel, pour a boiling mixture of 5 ml. water and exactly 1 ml. HCl slowly around the paper to dissolve all hydroxide and wash.

Swirl contents of flask to wash down particles of hydroxide, boil down to about 10 ml., cool, pipette 1 ml. KI solution into flask, titrate immediately by thiosulfate solution, in a 50-ml. Exax burette, until the yellow color is almost discharged. Pipette 1 ml. starch solution into flask and discharge progressively blue, purple, pink and straw colors.

[19] Phosphoric acid produces a precipitate of titanic phosphate, which obscures the thiocyanate end-point.

[20] By Lewis B. Skinner, Cons. Chem. and Met. Engr., Denver, Colorado. Ind. Eng. Chem., Anal. Ed. 3, 411, 1931.

Insert a glass tube, bent to hook on the rim of the flask and to conform to the side and terminating at the bulge, connected to a sodium bicarbonate wash bottle and a limestone and muriatic acid carbonic acid generator and pass CO_2 at the rate of about four bubbles per second, this to avoid air-oxidation.

Discharge color which may return by adding thiosulfate drop by drop until the solution remains colorless some fifteen minutes.

Titrations should be conducted over white surfaces and between the observer and a window.

Deduct the 0.1–0.2 ml. found in a blank consisting of 1 ml. HCl and the same volume of water, multiply the iron taken by its percentage of purity and by 1.4298 and divide by the milliliters used to obtain the value of the thiosulfate per ml. It should be equivalent to about 0.0005 g. Fe_2O_3.

Sodium Hydroxide Solution.—500 g. NaOH per liter, stored in ceresine-protected bottle.

Sodium Chlorate Solution.—300 g. $NaClO_3$ per liter.

Sodium Sulfide Solution.—200 g. $Na_2S \cdot 9H_2O$ per liter. For wash water, dilute 50 ml. to one liter.

METHOD A. SANDS LOW IN ALUMINA, ETC.

Run blanks; the aggregate of the iron in the reagents used is sufficient to vitiate results.

Procedure.—Weigh 10 g. of 100-mesh sand into a silver dish, add 100 ml. 48% C. P. HF (no sulfuric), evaporate to dryness, cool, add 10 ml. sodium hydroxide solution and 1 ml. sodium chlorate solution, evaporate to dryness, heat over naked gas flame to incipient redness and quiet fusion, run the melt around the sides of the dish until it solidifies, cool, add 100 ml. water, heat until disintegration takes place, transfer to 250-ml. beaker, scrub the dish first with water and then with 1 ml. HCl, add 10 ml. HCl and 1 ml. HNO_3 to make acid, boil, add a crystal of chlorate, boil again, cool somewhat, add ammonia in excess, boil, allow ferric hydroxide to settle a minute or so, filter through 9-cm. paper, wash, discard filtrate and handle the precipitate as in the case of standardizing.

Deduct the blank reading from that obtained, multiply by the value of the thiosulfate per ml. and move the decimal point one place to the right for per cent Fe_2O_3.

Should the run-down in the " copper " flask go to dryness, take up with 2 ml. water, 1 ml. HCl, a few drops of HNO_3, boil, dilute, filter off any insoluble residue, precipitate by ammonia and treat the ferric hydroxide as before. Merely adding HCl to dissolve the dried mass and then titrating will give too low results; the residue must be re-oxidized and the nitric acid must be removed by precipitation by ammonia and filtering.

METHOD B. SANDS CONTAINING SEVERAL PER CENT OF ALUMINA

Any proportionately high amounts of extraneous matter present with the ferric chloride prolong the time of titrating quite materially, so it is desirable to remove alumina. Further, alumina tends to prevent the volatilization of silica by reasonable amounts of HF, so residual silicic acid should be removed.

Procedure.—Proceed as in Method A up to fusion in silver dishes, except to use 20 ml. of sodium hydroxide, instead of 10 ml., and omit the sodium chlorate.

Transfer the disintegrated aqueous solution from the silver dish to a 400-ml. beaker, cleaning as before; add 3 ml. HCl to avoid tearing the filter paper later, dilute to 250 ml., add 10 ml. sodium sulfide solution, boil, cool, allow the solution to stand until the supernatant liquid is entirely free of a greenish color or is somewhat yellow, preferably over night; filter on a 11-cm. paper (pouring just a small amount of the solution around the paper at the start to "harden" it), wash with warm sodium sulfide water, set the filtrate aside to see whether or not any further precipitation occurs; transfer the precipitate from the paper to the beaker in which precipitation was made by wash bottle jet, place beaker beneath funnel, dissolve the black stain on the paper by a boiling mixture of 3 ml. HCl and 7 ml. water, this dissolving FeS but not necessarily Ag_2S; wash with hot water, boil the solution free of H_2S, Ag_2S not dissolving but FeS doing so, add 1 ml. HNO_3, thus dissolving Ag_2S, evaporate to dryness to dehydrate silicic acid, add 10 ml. of 1 : 1 HCl and 1 ml. HNO_3, boil, dilute to 100 ml., boil again, filter through a 9-cm. paper, breaking up clots of SiO_2, discard precipitate; add ammonia in excess to the filtrate and treat the ferric hydroxide precipitate as described before.

NOTES.—It is advisable to re-standardize the thiosulfate about every two weeks. Without sterilization the solution will change almost daily.

Complete ferric hydroxide separations cannot be made in the presence of organic matter from distilled water or any other source, nor by sodium hydroxide, because of the delicacy required.

For ordinary work 5 g. charges may be used, cutting down the amounts of reagents recommended proportionately.

Decomposition is complete as a result of the hydrofluoric rundown and the simple and expeditious fusion by sodium hydoxide.

The "copper" flask is made of glass, so-called because of its desirable form for making copper and other titrations as used in smelter laboratories of the West.

The sodium chlorate is used to eliminate organic matter, derived largely from ceresine in the hydrofluoric acid. In the sodium sulfide separation organic matter does not inhibit and it is not desired to convert ferrous to ferric iron, so the chlorate is omitted.

When boiling down in the copper flask with only one ml. of HCl present, no acid is eliminated even at a concentration of 10 ml., so dried specks which may have been caused by splattering of the solution should be dissolved by running the hot 10 ml. of HCl around the sides at the finish. Greater quantities of HCl prolong the straw color at the finish of the titration and give higher readings. The 1 ml. HCl is more than ample to take into solution any ferric hydroxide which may occur in analyzing glass sands.

By suitable minor modifications this method may be applied to the delicate determinations of iron in glass, clays, feldspars, barites, etc.

STANNOUS CHLORIDE METHOD FOR DETERMINATION OF FERRIC IRON

The procedure is based upon the reduction of the yellow ferric chloride to the colorless ferrous salt by stannous chloride, the following reaction taking place:

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

The method is of value in estimating the quantity of ferric iron in presence of ferrous, where the two forms are to be determined. In order to obtain the total iron the ferrous is oxidized by adding a few crystals of potassium chlorate and taking to dryness to expel chlorine, and then titrating with stannous chloride.

The accuracy of the method depends upon the uniformity of conditions of temperature, concentration, etc., of making the run with the sample and of standardizing the stannous chloride. The solution should be free from other oxidizing agents, or from salts that give colored solutions.

The amount of iron in terms of ferric oxide that can be estimated by this procedure ranges from 0.002 gram to 0.05 gram.

Reagents. *Stannous Chloride Solution.*—The reagent is prepared by dissolving 2 grams of stannous chloride crystals in hot concentrated hydrochloric acid and making up to 1 liter. The solution should be kept in a dark bottle to which the titrating burette is attached in such a way that the liquid may be siphoned out into this, as shown in the illustration, Fig. 58. The air entering the bottle passes through phosphorous or pyrogallic acid to remove the oxygen. In this way, protected from the air, the reagent will keep nearly constant for several weeks. It is advisable, however, to restandardize the solution about every ten to fifteen days. One ml. will be equivalent to about 0.001 gram Fe.

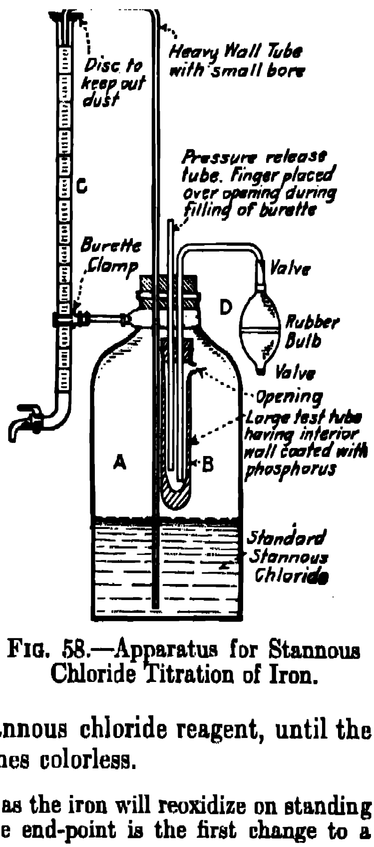


FIG. 58.—Apparatus for Stannous Chloride Titration of Iron.

Standard Iron Solution.—8.6322 grams of ferric ammonium alum is dissolved in dilute hydrochloric acid and made up to one liter. The iron is determined in 100-ml. portions by the dichromate method. One ml. will contain about 0.001 gram Fe.

Procedure.—To the sample in a casserole is added 25 ml. of concentrated hydrochloric acid and an equal volume of water. The resulting solution is heated to boiling and quickly titrated with the stannous chloride reagent, until the yellow color fades out and the solution becomes colorless.

NOTE.—The titration should be done quickly, as the iron will reoxidize on standing and the solution again become yellow. The true end-point is the first change to a colorless solution.

COLORIMETRIC METHODS FOR THE DETERMINATION OF SMALL AMOUNTS OF IRON

IRON TRACES. (THIOCYANATE METHOD[21]

Introduction.—By this method 1 part of iron may be detected in 50 million parts of water. The presence of free mineral acid increases the sensitiveness of the method, so that it is especially applicable to the determination of small amounts of iron in mineral acids. It is available in presence of many of the ordinary metals and in presence of organic matter. Silver, copper, cobalt, and mercuric chloride, however, interfere.

Nitric acid gives a color with thiocyanates that may be mistaken for iron.

This method, like the stannous chloride method, determines only the ferric iron. It is based on the fact that ferric ion and an alkali thiocyanate, ammonium or potassium, in an acid solution give a red color, the intensity of which is proportional to the quantity of iron present. With KCNS the color is due to the formation of the undissociated compound, $Fe(CNS)_3 \cdot 9KCNS \cdot 4H_2O$.

Reagents Required. *Standard Iron Solution.*—A ferric solution, the iron content of which has been determined, is diluted and divided so as to obtain 0.0004 gram Fe. This is made up to 2 liters with water containing 200 ml. of of normal ammonium thiocyanate solution, is used as a standard. One hundred ml. contains 0.00002 gram Fe.

Normal thiocyanate contains 76.1 grams of NH_4CNS per liter.

Procedure.—The weighed sample, 1 to 10 grams, or more if necessary, is dissolved in dilute H_2SO_4 and oxidized by adding dilute permanganate, $KMnO_4$, solution drop by drop until a faint pink color is obtained. The sample is diluted to exactly 100 ml. and is poured into a burette graduated to $\frac{1}{10}$ ml. Two colorless glass cylinders of the 100-ml. Nessler type are used for comparison of standard and sample. Into one cylinder is poured 100 ml. of the standard solution, made as directed above. Into the second cylinder containing 10 ml. of sulfuric acid with 10 ml. ammonium thiocyanate, NH_4CNS, diluted to 60 or 70 ml., the sample is run from the burette until the depth of the color thus produced on dilution to 100 ml. exactly matches the standard. From the number of ml. used the weight of the sample is calculated. One hundred ml. of the standard contains 0.00002 gram Fe.

Dividing the weight of iron in the standard by the weight of sample used and multiplying by 100 gives the per cent of iron in the sample.

NOTES.—If other metals are present that form two series of salts, they must be in the higher state of oxidation, or the color is destroyed. (Sutton.) Oxalic acid, if present, destroys the color. Oxidation with $KMnO_4$ or $KClO_3$ with subsequent removal of Cl_2 prevents this interference. (Lunge, Chem. News, 73, 250 (1896).)

Chlorides of the alkaline earths retard or prevent the thiocyanate reaction. (Weber, Chem. News, 47, 165 (1883).)

The colorimeter used for the determination of minute quantities of lead would serve admirably for the determination of traces of iron by the thiocyanate method.

Acids, hydrochloric or sulfuric (diluted), may be added directly to the ammonium thiocyanate solution.

[21] Thomson, J. Chem. Soc., 493 (1885), and Chem. News, 51, 259 (1885).

FERRON METHOD (7-IODO 8-HYDROXYQUINOLINE 5 SULFONIC ACID)[22]

A 0.2% aqueous solution of the reagent is used. The solution is made neutral to methyl orange paper. From 1 to 5 ml. of the reagent is added to the unknown which is made up to volume in a Nessler tube or colorimeter cup, and compared in the usual way with standards. The reagent solution has a bright yellow color; a concentration of 1 part of ferric iron in 10^7 parts of solution gives a perceptible change to green. The color is stable to light, but excess of acid or base destroys it. The solution may contain colorless ions, but should be free of large concentrations of colored ions or of ions that hydrolyze. Ferrous ion does not interfere; from 1.7–3 p.p.m. of Ni; 1.7 p.p.m. of Co; 0.3–1.5 p.p.m. of Cr does not interfer. Copper precipitates the reagent.

THIOGLYCOLLIC ACID METHOD[23]

The reagent, $HSCH_2COOH$, thioglycollic acid is a liquid. The solution to be tested should be neutral or very slightly acid and free of oxidizing agents. One drop of the reagent is added, then 0.5 ml. of conc. ammonium hydroxide, and the color developed is compared with that of a standard prepared under like conditions. The pinkish or purplish tint is due to a ferrous complex, and the reagent reduces ferric salts. One part of iron per 4 or 5 million of solution can be detected. The chief interfering ions are those of cobalt, nickel, manganese and uranium. If both ferric and ferrous iron are present, then the ferric ion may be determined by the thiocyanate or the ferron procedure in a portion of the solution, and the total iron by the thioglycollic procedure in a second portion of the solution.

SALICYLIC ACID METHOD FOR DETERMINING SMALL AMOUNTS OF IRON[24]

Salicylic acid produces an amethyst color with neutral solutions of ferric salts, the depth of the color being proportional to the concentration of the ferric iron in the solution. The reaction is useful in determining small amounts of iron in neutral salts, such as sodium, ammonium, or potassium alums, sulfates, or chlorides, zinc chloride, etc. Phosphates, fluorides, thiosulfates, sulfites, bisulfites and free mineral acids should be absent. The sample should not contain over 0.0002 gram iron, as the depth of color will then be too deep for colorimetric comparisons. As low as 0.00001 gram ferric iron may be detected. Ferrous iron produces no color with the reagents; hence the procedure serves for determining ferric iron in presence of ferrous.

The material is dissolved in 20 ml. of pure water, the sample filtered if cloudy, and transferred to a Nessler tube. Dilute potassium permanganate solution is added until a faint pink color is produced and then 5 ml. of a saturated solution of salicylic acid. (The reagent is filtered and the clear solution used.) Comparison is made with standard solutions containing known amounts

[22] Yoe, J. Am. Chem. Soc., 54, 4139 (1932).
[23] Lyons, J. Am. Chem. Soc., 49, 1916 (1927).
[24] $FeCl_3$ Colorimetric Method of Hostetter (J. Am. Chem. Soc., 41, 1531, 1919).

of ferric iron, the standards containing the same reagents as the sample. If desired the standard iron solution (0.086 gram ferric ammonium alum, clear crystals, dissolved in water containing 2 ml. of dilute sulfuric acid and made to 1000 ml.; each ml. contains approximately 0.00001 gram Fe‴) is added from a burette to 5 ml. of salicylic acid diluted to 25 ml. in a Nessler tube, until the color of the standard matches the sample. A plunger is used to stir the liquids.

TECHNICAL ANALYSIS OF IRON AND STEEL[25]

The elements carbon, manganese, phosphorus, sulfur, and silicon are invariable constituents of iron and steel, and are always included in an analysis. Copper and arsenic are sometimes found; aluminum, chromium, nickel, molybdenum, tin, titanium, tungsten, vanadium, and zinc occur in special alloy steels. Minute traces of oxygen, hydrogen, and of many other elementary constituents frequently are present, but are of so little importance that they are seldom considered in an analysis.

The importance of the subject has called for a special chapter on the subject of iron and steel. This may be found in Volume II of this work. The individual determinations are given in chapters throughout Volume I. We will deal with a few determinations here.

PREPARATION OF THE SAMPLE

The sample of borings is taken from several portions of the piece by a drill, free from oil or grease, and stored in a heavy manilla envelope. For carbon determinations samples contaminated by oil or grease should be thoroughly washed with ether before making the determination.

TOTAL CARBON

The determination is required for an accurate estimation of carbon where the color test indicates the carbon content outside the limits of requirement, or in cases where interfering substances are present. In material where the carbon content is of extreme importance, the color method is not used. Details of the procedure for determining carbon by direct combustion are given in the chapter on Carbon. The following procedure is recommended by the Bureau of Standards:

(a) **In Irons.**—Two grams of iron are mixed with about twice the weight of purified ferric oxide. The mixture is placed in a platinum boat, which is

[25] By W. W. Scott.

lined with a suitable bed material, and is burned in a current of oxygen, as described below.

(*b*) **In Steels.**—The method is the same as for irons with omission of the ferric oxide mixture.

Details of Direct Combustion Method. ***Furnaces and Temperature of Burning.***—Porcelain tubes wound with " nichrome " wire, provided with suitable heat insulation and electrically heated, are used, and readily give temperatures to 1100° C. Type FB 301 Hoskins tube furnace and the hinged type, are satisfactory. The temperature control is by means of an ammeter and rheostat in series with the furnace, with occasional check by a thermocouple.

Boats and Lining.—Platinum boats provided with a long platinum wire for manipulation in the tube are mostly used; alundum ones occasionally. The bed or lining on which the steel rests is 90-mesh " RR alundum, alkali-free, specially prepared for carbon determination." A layer of this alundum is also placed in the bottom of the combustion tube to prevent the boat sticking to the glaze. A platinum cover for the boat is sometimes used, and is essential when the combustion is forced.

The nature and quality of the bed material are matters of great importance. Alumina as prepared from the sulfate or from alum may not be free from sulfate or alkali, both of which have given serious trouble at the Bureau. The alkali, if present, may not manifest itself by an alkaline reaction until after one or two combustions have been made, using the same bed material. Even the ordinary white " alundum " on the market carries a few hundredths of 1% of alkali. Iron oxide has been tried, and when pure should, apparently, give good service. As yet, however, it has been difficult to obtain or prepare acceptable material for use with steels. Quartz sand gives rise to a fusible slag which, melting before combustion is complete, incloses bubbles of carbon dioxide gas. This defect would probably inhere in any other material of an acid character. The presence in the silica bed after combustion of crystals which appear to'be carborundum has occasionally been noted.[26]

Purity of Oxygen. Blanks.—Oxygen may be made electrolytically, whereby the content of this element is usually 99 to 99.5%, and sometimes higher. Even with this gas a slight blank is usually obtained. When running a blank, in addition to the usual precautions, the rate at which the oxygen is introduced should be the same as when burning a sample, and the time should be three to five times as long.

Method of Admitting Oxygen and Rate of Combustion.—The furnace being at the proper temperature, the boat containing the sample is introduced. Oxygen is admitted either at once or after the boat has reached the temperature of the furnace, as the operator prefers, or as the nature of the steel may demand. The rate of flow of the oxygen varies with the absorption apparatus used and with the preference of the operator, and may be considerably more rapid when absorbing carbon dioxide in soda lime than in an alkaline solution. A rapid flow of oxygen also facilitates the burning of resistant samples. A continuous forward movement of the gas current is maintained at all times. The time for a determination varies, of necessity, with the nature of the sample and the rate of flow of the oxygen, ranging from ten to thirty minutes. The endeavor

[26] Statement of Mr. George M. Berry, of the Halcomb Steel Co.

is to obtain a well-fused oxide. With all samples close packing in a small space is conducive to rapid combustion and to fusion of the resulting oxide.

Authorities differ as to the advisability of allowing the oxide of iron to fuse thoroughly. Even when fusion does take place additional carbon dioxide is obtained very frequently by grinding the oxide and reburning. Often more than one regrinding and reburning are necessary in order to reduce the amount of carbon dioxide obtained to that of the constant blank.

Oxides of sulfur have been found very difficult to eliminate from the gases leaving the tube. Lead peroxide ("nach Dennstedt") heated to 300° C. and zinc at room temperature appear to retain them best.

Attention is called to the inadmissibility of using dry agents of different absorptive power in the same train, in positions where a difference could possibly affect results.

Weighing of Tubes.—There is much greater difficulty in securing constant conditions when weighing absorption tubes than is usually considered to be the case. Electrical effects, caused by wiping as a preliminary to weighing, may occasionally cause errors in weight running into the milligrams. The use of counterpoises of equal volume and similar material and shape is recommended.

If tubes are weighed full of oxygen, care is necessary to secure a uniform atmosphere in them. Even though the attempt is made to keep the apparatus always full of oxygen, some air is admitted when the boat is pushed into the combustion tube, and a much longer time is required to displace this than is usually allowed, unless the flow of oxygen during aspiration is rapid. The same is true if the tubes are weighed full of air by displacing the oxygen left in them after the steel is burned. Another source of error may arise from the air admitted when putting the boat into the tube, if this air contains much carbon dioxide, as is the case when a gas furnace is used. The boat is usually pushed at once into the hot furnace, and as combustion begins almost immediately, there is no opportunity for displacing this air before the steel begins to burn.

GRAPHITE IN IRON

Two grams of iron are dissolved in nitric acid (sp.gr. 1.20), using 35 ml. and heating very gently. The residue is collected on an asbestos felt, washed with hot water, then with a hot solution of potassium hydroxide (sp.gr. 1.10), followed by dilute hydrochloric acid and finally by hot water. After drying at 100° C., the graphite is burned in the same manner as the total carbon, but without admixture of ferric oxide.

MANGANESE IN IRON AND STEEL

Ammonium Persulfate Method

Small amounts of manganese may be determined colorimetrically by the persulfate method, provided the sample does not contain over 1.5% of manganese.

Reaction.—$2Mn(NO_3)_2+5(NH_4)_2S_2O_8+8H_2O$

$$=5(NH_4)_2SO_4+5H_2SO_4+4HNO_3+2HMnO_4$$

One tenth to 0.2 gram of steel, according to the amount of manganese in the sample, is placed in a 10-in. test-tube and 10 ml. of nitric acid (sp.gr. 1.2) are added. The sample is heated in a water bath until the nitrous fumes are driven off and the steel is completely in solution. Fifteen ml. of $AgNO_3$ solution (1.5 g. per l.) are added to the cooled sample, followed immediately with about 1 gram of ammonium persulfate crystals. The solution is warmed (80 to 90° C.) until the color commences to develop, and then for half a minute longer, and then placed in a beaker of cold water until the solution is cold. Comparison is now made with a standard steel treated in the same way, the comparison being made exactly as indicated for determining carbon by the color method. See chapter on Carbon.

Example.—If the standard, containing 0.6% Mn, is diluted to 15 ml., each ml. = 0.04% Mn. If the sample required a dilution of 20 ml. to match the standard, then $0.04 \times 20 = 0.8\%$ Mn.

NOTE.—If preferred, the sample may be titrated with standard sodium arsenate, one ml. of which is equivalent to 0.1% on basis of 0.1 gram sample.

Lead Oxide Method (Deshey)

Oxidation of the manganese in the steel is effected in a nitric acid solution by addition of red lead (or by lead peroxide); the lead peroxide, formed, oxidizes the manganese nitrate to permanganic acid. The solution is now titrated with standard sodium arsenite, the following reaction taking place:

$$2HMnO_4 + 5Na_3AsO_3 + 4HNO_3 = 5Na_3AsO_4 + 3H_2O + 2Mn(NO_3)_2.$$

One fifth gram of steel is placed in a 150-ml. beaker and dissolved with about 30 ml. of nitric acid (sp.gr. 1.12). After violent action has subsided, the beaker is placed on a hot plate and when the iron has dissolved, 20 ml. of water added. The manganese is now oxidized by adding red lead in small portions at a time, until the solution appears brown with a pinkish purple foam on the surface. The solution is diluted with hot water until the volume is about 100 ml. and then boiled for a few minutes. It is now placed in a dark closet to cool. (A fresh batch of samples may be started in the meantime.) The solution is carefully decanted off from the peroxide, and with the washings of the peroxide residue, titrated with standard sodium arsenite to the yellowish green end-point. The sodium arsenite is made by dissolving 4.96 grams of pure arsenious acid together with 25 grams of sodium carbonate in 200 ml. of hot water and the solution diluted to 2500 ml. The arsenite is standardized against a steel sample of known manganese content, or against standard permanganate solution.

Bismuthate Method for Determining Manganese

(See also A. S. T. M. methods in Vol. 2)

This is the most accurate method for determining manganese in iron and steel. The procedure is as follows:

Procedure.—One gram of drillings is dissolved in 50 ml. of nitric acid (sp.gr. 1.135) in a 200-ml. Erlenmeyer flask. Iron should be filtered. The solution is cooled, about 0.5 gram of sodium bismuthate is added, and it is

then heated until the pink color has disappeared. Any manganese dioxide separating is dissolved in a slight excess of a solution of ferrous sulfate or sodium sulfite. The solution is boiled till free from nitrous fumes. After cooling to 15° C., a slight excess of bismuthate is added and the flask is shaken vigorously for a few minutes. Then 50 ml. of 3% nitric acid are added and the solution is filtered through asbestos. A measured excess of ferrous sulfate is run in and the excess titrated against permanganate solution which has been compared with the iron solution on the same day. A great many steels now carry small amounts of chromium as impurity. In such cases titration against arsenite solution is recommended, or removal of the chromium by zinc oxide and subsequent determination of the manganese by the bismuthate method.

Permanganate solutions are standardized against sodium oxalate.

DETERMINATION OF PHOSPHORUS

(See A. S. T. M. methods in Vol. 2)

(*a*) **Preparation of Solution and Precipitation of Phosphorus.**—Two grams of sample are dissolved in nitric acid (sp.gr. 1.135) and the solution is boiled until brown fumes no longer come off. Ten ml. of permanganate solution (15 grams to 1 liter) are added, and the boiling is continued. Sodium sulfite solution is added to dissolve the oxide of manganese, and the solution is again boiled and then filtered. With irons the insoluble residue should be tested for phosphorus. After cooling the filtrate, 40 ml. of ammonia (sp.gr. 0.96) are added, the solution is agitated, and when the temperature is at 40° C., 40 ml. of molybdate solution are added and the solution is shaken vigorously for five minutes. After settling out, the yellow precipitate is treated according to one of the following methods, *b* or *c*:

(*b*) **Alkalimetric Method.**—The precipitate is washed with 1% nitric acid solution followed by 1% potassium nitrate solution until the washings are no longer acid. The precipitate is dissolved in a measured excess of standardized sodium hydroxide solution and titrated back with standardized nitric acid using phenolphthalein. The solutions are standardized against a steel with a known amount of phosphorus.

(*c*) **Molybdate Reduction Method.**—The precipitate is washed ten to fifteen times with acid ammonium sulfate (prepared according to Blair) or until the washings no longer react for iron or molybdenum. It is dissolved in 25 ml. of ammonia (5 ml. ammonia of 0.90 sp.gr. to 20 ml. water). The filter is washed well with water and 10 ml. of conc. sulfuric acid added to the filtrate, which is run through the reductor at once and titrated against a N/30 permanganate solution which has been standardized against sodium oxalate.

GRAVIMETRIC METHOD. SULFUR BY OXIDATION

Five grams of iron or steel are dissolved in a 400-ml. Erlenmeyer flask, using 50 ml. of conc. nitric acid. A little sodium carbonate is added, the solution is evaporated to dryness, and the residue baked for an hour on the hot plate. To the flask 30 ml. of conc. hydrochloric acid are added, and the evaporation and baking are repeated. After solution of the iron in another

30 ml. of conc. hydrochloric acid and evaporation to a syrupy consistency, 2 to 4 ml. of the same acid are added, followed by 30 to 40 ml. of hot water. The solution is then filtered and the residue washed with hot water. The sulfur is precipitated in the cold filtrate (about 100 ml.) with 10 ml. of a 10% solution of barium chloride. After forty-eight hours the precipitate is collected on a paper filter, washed first with hot acid (containing 10 ml. of concentrated hydrochloric acid and 1 gram of barium chloride to the liter) until free from iron and then with hot water till free from chloride; or, first with cold water, then with 25 ml. of water containing 2 ml. of concentrated hydrochloric acid to the liter. The washings are kept separate from the main filtrate and are evaporated to recover dissolved barium sulfate.

The paper containing the insoluble residue above mentioned is put into a platinum crucible, covered with sodium carbonate free from sulfur, and charred without allowing the carbonate to melt. The crucible should be covered during this operation. Sodium nitrate is then mixed in and the mass fused with the cover off. An alcohol flame is used throughout. The melt is dissolved in water and evaporated, with hydrochloric acid in excess, to dryness in porcelain. The evaporation with water and hydrochloric acid is repeated to insure removal of nitrates. The residue is extracted with a few drops of hydrochloric acid and water, the insoluble matter is filtered off, and barium chloride is added to the filtrate. The barium sulfate obtained is added to the main portion.

Careful blanks are run with all reagents.

NOTE.—For volumetric method see chapter on Sulfur.

DETERMINATION OF SILICON

One gram of pig iron, cast iron, and high silicon iron or 5 grams of steel, wrought iron, and low silicon iron are taken for analysis. (By taking multiples of the factor weight 0.4693, SiO_2 to Si, the final calculation is simplified.) The sample is placed in a 250-ml. beaker and 20 to 50 ml. of dilute nitric acid added. If the action is violent, cooling the beaker in water is advisable. When the reaction subsides, 20 ml. of dilute sulfuric acid (1 : 1), are added, the mixture placed on the hot plate and evaporated to dense white fumes. The residue is taken up with 150 ml. of water containing 2 to 5 ml. of sulfuric acid and heated until the iron completely dissolves.

The solution is filtered and the silica residue washed first with hot dilute hydrochloric acid (sp.gr. 1.1), and then with hot water added in small portions to remove the iron sulfate. The residue is now ignited and weighed as silica.

If there is any doubt as to the purity of the silica, moisten the residue (in a platinum crucible) with conc. sulfuric acid and add a few ml. of hydrofluoric acid (crucible cover full), evaporate to dryness, ignite and weigh. The loss of weight is due to silica.

NOTE.—If the ash is colored by iron oxide, silica is determined by difference after expelling the silica by adding 4 to 5 ml. of hydrofluoric acid and a few drops of sulfuric, taking to dryness and igniting the residue.

The following acid mixtures are recommended by the U. P. Ry. For steel, wrought iron and low silicon iron, 8 parts by volume of HNO_3 (sp.gr. 1.42); 4 parts of conc. H_2SO_4

(sp.gr. 1.84); 6 parts HCl (sp.gr. 1.2), and 15 parts by volume of water. For dissolving pig iron, cast iron and high silicon iron, a mixture of 8 parts by volume of conc. nitric acid and 5 parts of conc. sulfuric acid, diluted with 17 volumes of water, is used.

Rapid Method for Determining Silicon in Foundry Work.—Liquid iron, dropped into cold water from a ladle 3 ft. above the water, will form shot in shapes depending on its chemical composition, silicon especially having a marked effect. Shot 1 to 3 in. in diameter, with concave upper surface, contain over 2% silicon. Flat or irregular shot contain low silicon, and shot with elongated tails contain very low silicon.

Other Methods for Determination of the Less Common Elements in Steel.—Other elements more commonly sought in alloy steel are copper, nickel, chromium, vanadium, tungsten, titanium and molybdenum. Methods for estimation of these elements are given in the chapters dealing with these substances. A.S.T.M. Methods for Steel may be found in Vol. 2.

Silicon.[22]—Dissolve twice the factor weight (2×.4693 g.) in 35 ml. mixed acid and evaporate to dryness. Take up with 10 ml. 1 : 1 HCl and 100 ml. water. Filter with suction and wash well with hot water and 1 : 1 HCl. Ignite to constant weight in a porcelain crucible.

$$\text{Wt.} \times 100 \div 2 = \%\ \text{Si}.$$

In some cases it is necessary to ignite in a platinum crucible and weigh the impure silica. This is then treated with a few drops of H_2SO_4 and HF. The difference in weight before and after treating is SiO_2. The Drown method or A. F. A. modification is also used.

Sulfur.[22]—A 5.0 g. sample is weighed into a 300-ml. flask and the flask fitted with thistle and extension tubes (see sketch). The extension tube is immersed in a 500-ml. beaker containing 200 ml. water and 20 ml. $CdCl_2$. Add enough 1 : 1 HCl to thistle tube to complete solution of drillings. Heat flask gently with a shielded burner until evolution is complete and steam passes over. Disconnect delivery tube and use as a stirring rod. Add 25 ml. HCl to beaker (or enough to dissolve the sulfide). Add 10 ml. fresh starch solution and titrate with standard iodine solution.

Phosphorus.[22]—Dissolve 0.2 g. drillings in 45 ml. 1 : 3 HNO_3. Add 5 ml. $KMnO_4$ solution (25 g. per liter) and boil 5 minutes. Clear the solution with sodium hyposulfite solution and boil 3 minutes. Add 40 ml. ammonium molybdate solution (see below) and NH_4OH in excess and shake well. Allow precipitate to settle at least 15 minutes. Filter on a Gooch filter with paper pulp and wash into a flask. Dissolve the ammonium phosphomolybdate with standard NaOH and titrate back with standard HNO_3, using phenolphthalein as indicator.

Ammonium Molybdate Solution.—(A) 120 g. MoO_3, 200 ml. H_2O, 200 ml. NH_4OH, 70 ml. HNO_3. To solution (A) add (B) 600 ml. HNO_3, 1300 ml. H_2O.

Manganese.[22]—Dissolve 0.3 g. drillings in 40 ml. 1 : 3 HNO_3. Oxidize with sodium bismuthate, avoiding great excess. Reduce with a small amount of sodium hyposulfite. Cool thoroughly and add an excess of sodium bis-

[22] Routine Methods of the Bethlehem Foundry and Machine Co. By courtesy of Mr. G. Thorp.

muthate. Filter on asbestos with suction and wash with 1 : 6 HNO_3. Titrate with standard sodium arsenite solution.

Nickel.[23]—Dissolve 0.5 g. drillings in 40 ml. 1 : 1 HCl and oxidize with 5 ml. HNO_3. Boil off all brown fumes and cool slightly. Add 50 ml. tartaric acid (20%) solution, make slightly ammoniacal and heat to boiling. Add 10 ml. dimethylglyoxime (10%) solution (either alcoholic or alkaline) for each 1% Ni present and heat gently for 15 minutes. Filter in a tared Gooch crucible prepared with asbestos, dry and weigh.

$$\text{Wt.} \times 0.20316 \times 100 \times 2 = \%\ \text{Ni}.$$

Chromium.[23]—Dissolve 1.0 g. drillings in 40 ml. 1 : 5 H_2SO_4. Oxidize with 5 ml. HNO_3 and add 5 ml. $KMnO_4$ (permanent solution of 25 g. per liter). Boil 15 minutes. Add carefully 40 ml. NH_4OH and boil 10 minutes. Add 20 ml. 1 : 1 H_2SO_4, cool somewhat, and filter on paper. Add standard $FeSO_4$ in excess and titrate back with standard $KMnO_4$ to a slight pink end-point.

Total Carbon.[23]—Weigh 0.5 g. drillings into a combustion boat filled with 120-mesh alundum and burn in a porcelain tube in an electric furnace. Oxygen is admitted through a H_2SO_4 wash bottle, an empty bottle and an "Ascarite" bottle in series. The products of combustion pass through a granulated zinc "U" tube and H_2SO_4 bulb into a modified Midvale absorption bulb filled with "Ascarite." This train is a modification of the Stetser and Norton apparatus. ("Ascarite" is a hydrated sodium-asbestos mixture.) The absorption bulb is weighed immediately before and after use.

$$\text{Wt. } CO_2 \times 0.2729 \times 2 \times 100 = \%\ \text{C}.$$

Graphitic Carbon.[23]—Dissolve 1.0 g. drillings in 35 ml. 1 : 3 HNO_3. Filter on asbestos, wash repeatedly with hot water. Ignite as above.

DETERMINATION OF TITANIUM, IRON AND SILICA IN ILMENITE[27] ($FeTiO_3$)

Apparatus. ***The Jones Reductor.***—The Jones reductor used for titanium reduction is a 1000-ml. burette. It is 2 in. in inside diameter and above the stop-cock is 20 in. long. The stem below the stop-cock is 6 mm. in inside diameter and is 5 in. in length. The stem is inserted in a No. 8 rubber stopper which also carries a short bent tube acting as an inlet tube for CO_2. The outlet tube is the side arm of a 1000-ml. suction flask.

The reductor is charged with about 900 g. of 20-mesh amalgamated zinc[28] supported on a one in. mat of glass wool. Then 500 g. of amalgamated zinc are added in sticks $2\frac{1}{2}$ in. in length and $\frac{1}{4}$ in. in diameter. The 20-mesh zinc should make a column of six in. in height and the stick zinc should increase the height to 12 in.

Solutions Required. ***Standard Ferric Ammonium Sulfate Solution.***—Dissolve 30 g. of $Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$ in 300 ml. of distilled water and 20 ml. of H_2SO_4 (1 : 1). Oxidize any ferrous iron that may be present by adding, drop by drop, a dilute solution of $KMnO_4$ to the first tinge of pink; then dilute to 1000 ml. and mix. Standardize by passing 100 ml. of the solution through the reductor as specified in the method for tita-

[27] Standard Method of the National Lead Company.

[28] Dissolve about 20 g. of mercury in 50 ml. of HNO_3 (1 : 1), dilute to a volume of 250 ml. with water and transfer to a stout 1000-ml. flask. Add to it 1800 g. of zinc and shake for a minute or two. Pour off the solution, wash thoroughly with tap water and finally with distilled water.

nium and titrate with standard $KMnO_4$ solution whose iron value has been ascertained. Run a blank and make correction for same. Calculate the value of one ml. in terms of iron. The iron value multiplied by 1.4344 gives the value in TiO_2. The iron value multiplied by 0.86139 gives the titanium value.[29]

Potassium Thiocyanate Indicator.—Make up a saturated solution.

Sulfuric Acid Wash Water.—To 1000 ml. of cold distilled water add 50 ml. of H_2SO_4 (sp.gr. 1.84).

Standard $KMnO_4$ Solution.—Dissolve 3.16 g. of $KMnO_4$ and make up to 1000 ml. with distilled water. Standardize [30] against Bureau of Standards sodium oxalate and calculate to terms of iron.

PREPARATION OF THE SAMPLE

Sample out about 40 g. of the ore which has been ground to pass a 100-mesh sieve. Mix thoroughly, weigh out about 5 g. and grind to an impalpable powder in an agate mortar. Mix thoroughly.

A. Determination of Titanium [31]

Method.—Weigh out 0.5 g. of the finely ground sample, brush into 250-ml. beaker and add about 5 ml. of water. Agitate to spread the sample over the bottom of the beaker and add 25 ml. of HCl (sp.gr. 1.18); digest on the water bath over night. From time to time stir to prevent residue from adhering to the beaker. If any residue has already done so, loosen by means of a glass rod. When decomposition has finally taken place, add 20 ml. of H_2SO_4 (sp.gr. 1.84) and evaporate to fumes of SO_3 and fume for two hours. Cool, dilute with 100 ml. of distilled water and heat on the hot plate for 45 minutes; add hot water from time to time to keep the volume constant. When the iron and titanium sulfates are completely in solution, filter, wash several times with hot H_2SO_4 wash water and finally with hot distilled water. Reserve the filtrate.

Transfer the residue to a No. 2 R.B. porcelain crucible, dry, ignite over a flame, add 15 g. of $K_2S_2O_7$ and fuse. Start the fusion over a low flame,[32] gradually increasing the heat as the fusion progresses. When the full strength of the flame has been attained, continue heating for 20 minutes. Cool, leach out with 50 ml. of water to which 10 ml. of H_2SO_4 (1 : 1) has been added; filter and wash. Combine with the main filtrate and bring to boiling.

Set the reductor in the mouth of the suction flask and clean by filling with hot dilute H_2SO_4 (1 : 4); allow the solution to remain a few minutes, then draw off and wash several times with distilled water. Titrate the cleanings with

[29] Titanium sulfate is oxidized by ferric sulfate according to the following reaction:
$Ti_2(SO_4)_3 + Fe_2(SO_4)_3 = 2Ti(SO_4)_2 + 2FeSO_4$.
The valence change in iron is one; therefore its chemical equivalent value is 55.84.
The valence change in titanium is one; its chemical equivalent value is 47.9.
Hence to convert iron values to titanium values multiply by 47.9/55.84 = 0.85781.

[30] A ferrous salt is oxidized by $KMnO_4$ according to the following reaction:
$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4) + 2MnSO_4 + K_2SO_4 + 8H_2O$.
The valence change in iron is one; hence its chemical equivalent value is 55.84.
The chemical equivalent value of $Na_2C_2O_4$ is 67.
Should 0.2 g. of $Na_2C_2O_4$ require 30 ml. of $KMnO_4$ solution, 1 ml. of $KMnO_4$ solution = 0.2/.30 = 0.00667 × 55.84/67 g. of iron.

[31] Both titanium and iron may be run on the same portion. See B.

[32] If started at too high a temperature, the melt will froth over the top of the crucible.

standard $KMnO_4$ solution to the first tinge of pink. If they take more than two or three drops of $KMnO_4$ solution, repeat until the desired result is obtained.

When the reductor is thoroughly cleaned, fill it just above the 20-mesh zinc with hot H_2SO_4 wash water, add the hot solution containing the titanium and wash the beaker with hot water.[33] Allow the solution to remain in the reductor at least 20 minutes. While the titanium is being reduced, displace the air in the flask with CO_2.[34] When the titanium is reduced and the air in the flask has been displaced, allow the solution to pass into the suction flask until the level of the liquid is just above the surface of the 20-mesh zinc;[35] then add 100 ml. of hot H_2SO_4 wash water and allow to drain as before. Finally wash four times with hot distilled water, allowing the washings to drain each time to just above the 20-mesh zinc before making another addition of the wash water. Keep a continuous flow of CO_2 passing at the rate of two bubbles per second.

Disconnect, add 5 ml. of the KCNS indicator and titrate[36] with the standard ferric alum solution to the first tinge of a light wine color. An additional 0.1 ml. of the standard should give a pronounced wine color. Take the first reading.

Run a blank determination and make correction for same.

Calculate to titanium content.

Accuracy.—Duplicate titrations should not disagree more than 0.1 ml.[37]

B. Determination of Total Iron

Method.—Proceed as described in "A" up to the stage where reduction is made. Instead, however, of adding the KCNS indicator and titrating with ferric alum solution, titrate at once with standard $KMnO_4$ solution to the first permanent tinge of pink.[38] Run a blank determination and correct accordingly.

Calculate[39] to per cent of iron.

$$0.0056 \times 23.91 \times 2 \times 100 = 26.78\%.$$

See footnote, method C.

[33] The solution in the reductor at this stage should just cover the upper surface of the zinc column.

[34] The CO_2 is most conveniently supplied by tapping a cylinder of the liquefied gas.

[35] Do not at any time during the reduction and washing allow the solution to get below the upper level of the 20-mesh zinc; air will get into the flask and oxidize the reduced titanium.

[36] Do not agitate until near the end of the titration.

[37] Ilmenite is usually free from interfering metals, such as copper, arsenic, antimony, etc. When present, remove them by passing H_2S through the acid solution. Filter, wash, boil to expel H_2S, oxidize with 10 ml. of 3% H_2O_2 and then continue boiling for 20 minutes longer to expel the H_2O_2. Cool somewhat and add a slight excess of $KMnO_4$ solution to destroy any H_2S or H_2O_2 that may remain. The solution after heating again is ready for the reductor.

[38] Both iron and titanium may be determined on the same portion. After determining the iron, transfer the solution to a large-sized beaker and evaporate down to a volume of 100 ml.; cool, dilute to 400 ml. with distilled water, bring to boiling and then put through the reductor and determine titanium. Where the time factor is not paramount, this procedure should be followed, as considerable labor is saved thereby.

[39] Both iron and titanium are titrated by the $KMnO_4$ solution. The method of calculating for iron content is best shown by the following example.

Let the titration require 55 ml. of $KMnO_4$ solution.

And let 1 ml. of $KMnO_4$ solution = 0.0056 g. of iron.

Let the titanium content be 30%.

If 1 ml. of $KMnO_4$ solution = 0.0056 g. of iron,

Accuracy.—Duplicate titrations should not disagree more than 0.15 ml.[40]

C. Determination of Ferrous Iron[41]

Apparatus.—In the mouth of a 500-ml. wide-mouth Erlenmeyer flask, set a glass funnel. The stem of the funnel should reach half way down the flask. Place in the funnel a 5-ml. pipette; the upper stem above the bulb should be about 2 in. long. The lower end of the pipette should be just above the solution when liquid is in the flask.

Method.—Weigh out 0.5 g. of finely ground sample and brush into the flask. Set funnel and pipette in place, connect the upper end of the pipette with a CO_2 generator and displace the air in the flask with CO_2.[42] When the air has been displaced, raise the pipette slightly and pour through the funnel 20 ml. of HCl (sp.gr. 1.18) and 50 ml. of H_2SO_4 (1 : 1). Set the pipette back in place and heat on gauze over a low flame until the ore is completely decomposed. Avoid excessive heating;[43] decomposition should take place in about 7 minutes.

Cool, add 100 ml. of cold distilled water, again cool and titrate with the standard $KMnO_4$ solution to the first tinge of pink. Calculate to FeO.[44]

Run in duplicate.

D. Determination of Silica

Method.—Weigh out 1.0 g. of the finely ground ore,[45] brush into a 250-ml. beaker and treat as described in "Method A" through the filtering off of the residue. Discard the filtrate (No. 1). Transfer the residue to a 15-g.

Then 1 ml. of $KMnO_4$ solution = $(0.0056 \times 0.85781) = 0.00479$ g. of titanium.

The titanium in 0.5 g. of ore is $30 \times 1/100 \times \frac{1}{2} = 0.15$ g., which will require $0.15 \times 1/0.004824 = 31.09$ ml. of the $KMnO_4$ solution.

The iron requires $(55.0-31.09) = 23.91$ ml. of the $KMnO_4$ solution.

∴The iron content of the ore is

$$0.0056 \times 23.91 \times 2 \times 100 = 26.78\%.$$

See footnote, method C.

[40] For the removal of impurities such as copper, arsenic, antimony, etc., see footnote, method A.

[41] Method of L. E. Barton.

[42] Keep CO_2 passing through the system during the whole course of the determination.

[43] If the solution is evaporated too far, low results will be obtained.

[44] Also calculate to Fe_2O_3. This may be done as follows:

Suppose the ore to contain 10% of FeO and 26.78% of total iron (see footnote, method B).

The ore will therefore contain:

$$10 \times \frac{55.84}{71.84} = 7.77\% \text{ of Fe as FeO},$$

$$26.78 - 7.77 = 19.01\% \text{ of Fe as } Fe_2O_3,$$

$$19.01 \times \frac{159.68}{111.68} = 27.18\% \text{ of } Fe_2O_3.$$

[45] When the titanium and iron content is low, the determination may be made on this 1-g. portion, in which case filtrates No. 1 and No. 2 may be used. The second filtrate, however, contains HCl. To remove it, precipitate the titanium and iron with NH_4OH (sp.gr. 0.9), boil, filter and wash. Dissolve the precipitate with 10 ml. of hot H_2SO_4 (1 : 2) and transfer to the main filtrate. Warm and proceed as described in "Method A." See also "Method B."

platinum crucible, dry and ignite over a Bunsen flame. Cool, add 5 g. of Na_2CO_3; mix, cover with 2 g. of Na_2CO_3 and fuse for thirty minutes. Cool, transfer to a 300-ml. porcelain casserole; leach out with 100 ml. of water, remove the crucible, police it, and wash. Transfer washings to the main solution, make acid with HCl (sp.gr. 1.18) and evaporate to dryness. Bake over a low flame on the hot plate to dehydrate the silica. Cool, add 20 ml. of HCl (sp.gr. 1.18) and heat to dissolve any oxides of iron and titanium that may be present, dilute to a volume of 150 ml., boil, filter and wash with hot distilled water. Discard the filtrate (No. 2). Transfer the precipitate to a 15-g. platinum crucible, dry on a hot plate, heat over a low flame until the paper is completely charred,[46] and then over the full flame until the paper has been completely removed. Cool in a desiccator and weigh. Add 6 ml. of HF and two or three drops of H_2SO_4 (sp.gr. 1.84); evaporate on a hot plate to dryness; ignite over a flame to drive off the last traces of H_2SO_4; cool and weigh. Repeat with 2 ml. of HF and a drop or two of H_2SO_4 (sp.gr. 1.84).

The loss in weight is SiO_2.

Accuracy.—Duplicate determinations should agree within 0.10%.

[46] Do not allow the paper to ignite over flame.

LEAD[1]

Pb, ***at.wt.*** **207.21;** ***sp.gr.*** **11.34;** ***m.p.*** **327.5°;** ***b.p.*** **1620° C.;** ***oxides,*** **Pb_2O, PbO, Pb_2O_3, Pb_3O_4, PbO_2**

The occurrence of lead in native state is rare and in comparatively small amounts. It occurs combined in a large number of minerals, principally as sulfide in galenite (galena), PbS. Among the other more common minerals: the carbonate, cerussite, $PbCO_3$; the sulfate; anglesite, $PbSO_4$; the phosphate, pyromorphite, $Pb_4(PbCl)(PO_4)_3$; minium, Pb_3O_4; wulfenite, $PbMoO_4$; crocoite, $PbCrO_4$. Also sulfo-salts, silicates, vanadates, arsenate, etc. Galena, the chief source, is frequently associated with marcasite (white iron pyrites), zinc blende (sphalerite), ZnS and pyrite, FeS_2.

DETECTION

In cold, sufficiently concentrated solutions containing HCl lead precipitates as $PbCl_2$, white, accompanied with silver and mercurous chloride, if these are present. It is distinguished from silver and mercury by its solubility in hot water (solubility at 100° C. three times that at 20° C.).

Potassium chromate precipitates yellow $PbCrO_4$ when added to a neutral or faintly acetic acid solution of lead. The precipitate dissolves in free mineral acids. The mineral acid may be neutralized by sodium or ammonium acetate.

Sulfuric acid precipitates $PbSO_4$, white. The sulfate is soluble in hot concentrated HCl, HNO_3 or H_2SO_4. It is soluble in sodium or ammonium acetates, sodium thiosulfate. The solubility in water is decreased by addition of a little H_2SO_4 or by presence of an appreciable amount of alcohol.

Hydrogen sulfide precipitates PbS, black, when added to a solution containing lead. Traces of lead may be detected in presence of 1 ml. HCl (sp. gr. 1.19) per 100 ml. of solution. Three times this acidity, however, has an

[1] Lead was employed by man many centuries ago as is shown by the objects made of this metal that have been found in ancient ruins. It was employed as a roofing material during the Medieval Ages. It was used during the early periods and is still used for manufacture of pipes. It is employed in storage batteries, covering of cables, in chemical industries—lead chambers in sulfuric acid manufacture, lead crystallizing pans etc.; it is employed in making shot and rifle bullets, and in alloys—pewter, type metal, Babbitt, and solder. Compounds of lead are extensively used—paint pigments, drying agents for oils, lead glass, plumber's cement, covering of steel to prevent rusting and many other purposes. All lead compounds are cumulative poisons.

appreciable effect on precipitation, as PbS is soluble in HCl or HNO_3 solutions stronger than 0.3 N. The test is best made in HCl solutions. (*Caution:* other members of the H_2S group should be absent.)

Sodium carbonate will transpose $PbSO_4$ to $PbCO_3$ forming a precipitate easily soluble in hot dilute acid solutions. Spongy metallic lead may be precipitated from the solution by zinc.

General Procedure.—Lead is precipitated from a slightly acid solution as PbS, black. PbS is separated from As, Sb, Sn by its comparative insolubility in $(NH_4)_2S_x$; from HgS by its solubility in dilute HNO_3 and is converted to $PbSO_4$ by heating to fuming with H_2SO_4, separating it from Bi, Cu and Cd. The $PbSO_4$ is converted to acetate by action of ammonium acetate, from which $PbCrO_4$, yellow, is precipitated by a soluble, neutral chromate (K_2CrO_4, $K_2Cr_2O_7$ etc.).

ESTIMATION

In addition to the valuation of ores, such as galena, PbS, etc., the determination of lead is required in a large number of substances of commercial importance. It is determined in lead mattes; certain slags; drosses from hard lead; cupel bottoms; lead insecticides (arsenate of lead, etc.); paint pigments (white lead, red lead, yellow and red chromates, etc.); it is determined in alloys such as solder, type metal, bell metal, etc. Its estimation is required in the analysis of a large number of ores, especially in minerals of antimony and arsenic. Traces of lead are determined in certain food products, where its presence is undesirable. Its use in the industry makes its determination of special importance.

If the ore is decomposed by HCl some of the lead may remain with silica and be volatilized as the chloride. That remaining in solution, unless provided for, will precipitate with the ammonia precipitate and will be reported as alumina. If H_2SO_4 is used in the decomposition of the ore, lead will remain with the silica as $PbSO_4$.

PREPARATION AND SOLUTION OF THE SAMPLE

In dissolving the ores, alloys or the metal lead, the following facts should be kept in mind. The metal is soluble in hot dilute nitric acid. Lead nitrate is comparatively insoluble in concentrated nitric acid, but dissolves readily upon dilution with water. Decomposition of an ore may generally be effected by treating with HNO_3 (1 : 1). (If HCl or HNO_3 is used, as may be advisable with certain sulfides, it is necessary to expel these acids with H_2SO_4 taking to fumes, cooling, adding a little water and again evaporating to fumes, otherwise

low results will be obtained.[2]) In the process of analysis the lead is left with the residue, which may contain, in addition to the silica, $BaSO_4$, tin and antimony salts, which persist in holding up lead, preventing its complete solution in ammonium acetate. The National Lead Company employs fusion with Na_2CO_3, leaching, filtering off the $PbCO_3$ and $BaCO_3$, dissolving in HCl, heating to expel CO_2, and precipitating PbS with H_2S.

Oxides and Carbonates.—These are generally soluble in dilute nitric acid. Hydrogen peroxide, sodium nitrite, etc. must be added to dissolve lead peroxide or red lead.

Sulfides.—It is often desirable to start with HCl to expel H_2S and follow this with HNO_3 or a mixture of HNO_3 and H_2SO_4; in any case taking to fumes with H_2SO_4. (See discussion above.) The residue may be extracted with ammonium or sodium acetate to dissolve $PbSO_4$. In presence of $BaSO_4$, a fusion, as given under the discussion above may be advisable.

Silicates and Slags.—These are decomposed by fusion with Na_2CO_3 and K_2CO_3, extracting the mass with water (traces of lead may dissolve), and converting the $PbCO_3$ formed to the nitrate, or to the chloride according to directions stated above. If preferred the ore may be treated with HF and H_2SO_4, taken to fumes to expel silicon tetrafluoride and the lead determined in the residue.

Alloys.—These are best decomposed by treatment with dilute nitric acid. The lead may then be converted to sulfate as in case of the ores. Specific details are given in the body of the text. Alloys of lead, antimony, tin and copper may be decomposed by the following method, which avoids formation of insoluble oxides of antimony and tin. A 0.5 gram sample is digested with 10 ml. of concentrated H_2SO_4 until a clear solution is obtained or at least until there is no residue of unattacked metal. The solution is cooled and then diluted with about 100 ml. of dilute (1 to 4) H_2SO_4. Five ml. of concentrated HCl are added. The solution is brought to a boil, allowed to cool and stand 4 hours. Lead is precipitated as sulfate and the antimony, tin and copper remain in solution. On the class of sample indicated, the lead sulfate may be determined gravimetrically.

SEPARATIONS

General Procedure for Separation of Lead. Separation as Lead Sulfate.—Lead may be separated from a number of elements whose sulfates are soluble in water and dilute acid solutions by conversion to the sulfate, $PbSO_4$. Barium, columbium, silica, tantalum, and tungsten accompany lead. Antimony, bismuth and silver may contaminate the lead sulfate and occasionally chromium and nickel may be found with this residue. In the presence of much bismuth or iron it is necessary to wash the residue with 10% sulfuric acid solution to keep the bismuth in solution and to prevent the formation of the difficultly soluble basic ferric sulfate. In absence of these contaminating substances, lead sulfate is best separated by adding to the dilute sulfuric acid solution an equal volume of alcohol before filtering to prevent a slight amount of the lead from dissolving, which would otherwise occur.

[2] Communicated to the editor by W. J. Brown, Chief Analyst, National Lead Company.

Separation of Lead from the Acid Insoluble Residue—Extraction of Lead by Ammonium Acetate.—Lead may be completely separated from silica, barium, tin and antimony by extraction with ammonium acetate, provided a sufficient amount of this reagent is used. Separation from barium sulfate may be effected even when the amount of barium is 100 times that of lead.[3, 4] Calcium, if present in the solution, will also be extracted to a considerable extent and will accompany the lead. Free sulfuric acid must be absent as it retards the extraction and will prevent this entirely if it is present to the extent of 10%. In the separation of lead from silica the presence of free acetic acid is desirable (20 g. of ammonium acetate and 3 ml. of 80% acetic acid per 100 ml. of extraction solution). Occasionally it is well to remove the silica by HF and H_2SO_4 treatment prior to the extraction of the lead. The filter containing the impure sulfate, obtained by one of the procedures for solution of the sample, is placed in a casserole and extracted with about 50 ml. of hot, slightly ammoniacal ammonium acetate, the stronger the acetate the better. The clear liquid is decanted through a filter and the extraction repeated until the residue is free from lead (i.e., no test is obtained for lead with $K_2Cr_2O_7$). A very effective method of extraction is by adding solid ammonium acetate directly to the sample on a filter and pouring over it a hot solution of ammonium acetate.

Lead sulfate containing arsenic should be dissolved in ammonium acetate, the extract made alkaline and lead precipitated as PbS. Arsenic remains in solution.

Ammonium Carbonate Method.—Lead may be separated from barium sulfate by digesting the mixed sulfates with ammonium carbonate solution, whereby the lead sulfate is transposed to lead carbonate and ammonium sulfate, while barium sulfate is not changed. The soluble ammonium sulfate may be washed out with ammonium solution followed by water. Since lead carbonate is slightly soluble in the ammonium salt, the filtrate is treated with hydrogen sulfide and the dissolved lead recovered as PbS. The residue containing lead carbonate and barium sulfate is treated with dilute nitric or acetic acid. Lead passes into solution, while barium sulfate remains insoluble.

Separation of Lead from Calcium.—Calcium, if present, will accompany lead in the acetate extract. The acetate solution of lead and calcium is evaporated to fumes with H_2SO_4. The cooled residue is taken up with water and NaOH added to dissolve the lead. The extract is filtered from calcium and lead determined in the filtrate, acidified with HCl.

If antimony is present, $PbSO_4$ carries down an appreciable amount of this element. Consult the section on pig lead, Vol. II.

Hydrogen Sulfide Method.—Separation from Barium, Columbium, Tantalum and Members of the *Ammonium Sulfide, Ammonium Carbonate and Water Soluble Groups.*—Lead sulfide is precipitated from an acid solution containing tartaric acid.

Separation from Tungsten.—Advantage may be taken of the solubility of tungstic acid in ammonia and ammonium tartrate. Lead as sulfate remains in the residue. Any entrained lead in the tungsten filtrate may be precipitated as sulfide by H_2S, keeping the solution alkaline with NH_4OH.

[3] W. W. Scott and S. M. Alldredge, Ind. Eng. Chem., Anal. Ed. 3, 32, 1931.
[4] 95% of the Pb is extracted when the ratio of Pb : Ba is 1 : 100.

Notes on Solution and Separation of Lead.[5]—It is a good practice to effect solution with dilute HNO_3 (1 : 1) and proceed as directed in "Determination of Lead in an Ore." When the nature of ore is such as to necessitate the use of HCl, fume, cool, take up with a few ml. of water, fume again and repeat this operation. It has been our experience that HCl may not be expelled by a single fuming and unless it is, low results are obtained.

Another cause for low results is the pernicious habit $BaSO_4$ and separated tin and antimony compounds have for holding up lead after the $PbSO_4$ has been treated with ammonium acetate. We separate the occluded lead from barium by a fusion with Na_2CO_3 and K_2CO_3, leach, filter off the $BaCO_3$ and $PbCO_3$, dissolve in HCl and boil to expel CO_2. The solution is neutralized with NH_4OH and then made acid with acetic; H_2S is passed to precipitate the lead. The occluded lead is separated from tin and antimony by a fusion of the treated residue with S–Na_2CO_3 mixture. After leaching, the tin and antimony are found in solution while the lead is present in the residue as PbS.

A cause for high results is the use of the theoretical factor 0.641 for the conversion of $PbCrO_4$ to Pb when the precipitate is heated to 100° C. and even to 110° C. An alloy having a lead content of 85% will invariably total 0.4% too high and examination of the $PbCrO_4$ will show the presence of water. For this reason, we use the factor 0.6375, which is constant for all weights of precipitate.

GRAVIMETRIC METHODS

DETERMINATION OF LEAD AS LEAD SULFATE

This method is generally considered among the best of the gravimetric methods for the determination of lead.

Solutions Required. *"Lead Acid."*—Mix 300 ml. of H_2SO_4 (sp. gr. 1.84) and 1800 ml. of distilled water. Dissolve 1 g. of c.p. lead acetate in 300 ml. of distilled water and add this to the hot solution, stirring meanwhile. Let stand 24 hours and filter through a thick asbestos pad.

Dilute Alcohol for Washing.—Mix equal parts of denatured alcohol and distilled water.

Procedure for Ores.—The material is brought into solution according to the procedure outlined under the preparation and solution of the sample, the lead precipitated as $PbSO_4$ by addition of an excess of sulfuric acid, nitric or hydrochloric acid expelled by taking to fumes (H_2SO_4) and the impure sulfate filtered off and washed, first with water containing 10% of its volume of H_2SO_4 until free of soluble impurities, and then with 50% alcohol solution to remove the free acid.

Purification.—The lead sulfate is dissolved from the impurities of the residue by repeated extraction with a strong solution of ammonium acetate. The separation from barium sulfate is complete,[6] very little SiO_2 dissolves, calcium,

[5] W. J. Brown, Chief Analyst, National Lead Company.
[6] S. M. Alldredge—Research, Univ. So. Calif., 1930.

if present, will accompany lead. The acetate solution is evaporated to dryness, taken up with water and a large excess of sulfuric acid added. Lead sulfate is again filtered and washed as before. Water is expelled by heating to 110° C. or by gentle ignition.

$$PbSO_4 \times 0.6833 = Pb.$$

NOTE.—In presence of Ca, Bi, Si, W, Cb, Ta, Ba, Sb, Ag, washing with dilute alcohol will not remove these completely. The solubility of $PbSO_4$ is increased by the presence of HCl and HNO_3, hence the necessity for their removal.

In determining lead in alloys the sulfate precipitation generally gives $PbSO_4$ as a difficultly soluble salt free from impurities. In case of ores, however, SiO_2 will be present and an acetate extraction of the $PbSO_4$ is necessary (100 ml. of a saturated solution of ammonium acetate will dissolve a little over 3 grams of $PbSO_4$). The $PbSO_4$ is reprecipitated from the extract, after diluting with water, by adding a large excess of H_2SO_4 (acidity should be 10% H_2SO_4).

Procedure for Determination of Lead in Alloys.—In a covered 300-ml. Erlenmeyer flask dissolve 1 g. of the alloy in 20 ml. H_2SO_4 (sp. gr. 1.84); heat the solution nearly to boiling until the metal is completely decomposed and the $PbSO_4$ is white (this may take 30 minutes or more) and finally boil for several minutes. Allow to cool, but not below 60° C., and then add slowly 50 ml. of water while the solution is agitated. Heat to boiling for several minutes in order to insure complete solution of antimony sulfate. Allow the $PbSO_4$ to settle out until the solution is clear, not letting the temperature fall below 60° C. If the liquid does not clear quickly, it must be heated longer. When clear, pour the solution through a weighed porcelain Gooch crucible with asbestos mat, decanting the solution as completely as possible without allowing more than a very small amount of $PbSO_4$ to go over into the crucible. Now add 10 ml. more of H_2SO_4 (sp. gr. 1.84) to the $PbSO_4$ in the original flask, and boil for several minutes. Cool, add slowly 30 ml. of water, and again heat to boiling for a few minutes; allow the solution to cool to about 60° C. and completely transfer the $PbSO_4$ to the Gooch crucible. Wash the precipitate with "lead acid" reagent.[7] Remove the beaker containing these solutions and wash out the "lead acid" with dilute alcohol; set the Gooch crucible inside a porcelain crucible; dry and ignite for five minutes over a Meker or Bunsen burner; cool and weigh as $PbSO_4$, which contains 68.33% lead.

NOTES.—Copper alloys are best decomposed by nitric acid, followed by sulfuric acid. The greater part of the acids are expelled by concentration to strong fumes, the solution is cooled and diluted with water. In presence of lead, $PbSO_4$ remains as a precipitate while copper, tin and zinc are in solution.

[7] Washing the lead sulfate with "lead acid" prevents the solution of $PbSO_4$ by the wash solution.

DETERMINATION OF LEAD AS THE MOLYBDATE, $PbMoO_4$

This method is rapid and has the following advantages:

a. The sulfation of lead is avoided. *b.* The acetate extraction is eliminated. *c.* The precipitate may be ignited. *d.* The ratio of lead to its molybdate compound is less than either lead to $PbSO_4$ or to $PbCrO_4$, lessening the magnitude of error through weighing.

Cobalt, calcium, strontium and barium have little effect in presence of ammonium acetate. In absence of this salt they interfere slightly.

The solution should be free from CrO_4, AsO_4, PO_4, Ti and Sn.

Procedure.—The ore or alloy is decomposed with nitric acid or aqua regia as the case may require. (Silica if present is eliminated by taking to dryness, dehydrating, taking up with dilute nitric acid and filtering.) To the clear liquid, 2 g. of ammonium chloride are added and then sufficient ammonium acetate to destroy the excess of free nitric acid, i.e., 2 g. per ml. of free HNO_3 present.

Lead is now precipitated by adding 40 ml. of ammonium molybdate solution (4 g. per liter + 10 ml. acetic acid), per 0.1 g. of lead present, stirring the mixture during the addition. After boiling for two or three minutes the precipitated lead molybdate is allowed to settle, then filtered and washed with small portions of hot water containing 2% of ammonium nitrate and ignited over a Bunsen burner to dull red heat.

The cooled residue is weighed as $PbMoO_4$. $PbMoO_4 \times 0.5643 = Pb$.

NOTES.—If antimony or other members of the group are present in the original sample, it is advisable to dissolve the residue in HCl and reprecipitate the lead with molybdate reagent.

If lead is in the form of the sulfide, as may be the case in a complete analysis of a substance, it is decomposed with hot dilute HNO_3 and precipitated as $PbMoO_4$.

Galena is best decomposed by treating with hydrochloric acid to expel sulfur as oxidation of sulfur to sulphate is not desirable in this method. If lead sulfate has formed due to oxidation of sulfur, it is advisable to treat any residue, remaining from the acid extraction, with ammonium acetate, adding the acetate extract to the solution containing the lead.

The sample, evaporated to dryness, is treated with about 10 ml. of dilute nitric acid (1 : 1) and a little water then heated and filtered. About 2 grams of ammonium chloride are added and for each ml. of free nitric acid (sp. gr. 1.42) two grams of ammonium acetate are necessary (total 10–15 g.). The precipitate generally appears a light canary yellow or yellowish white.

Washing the precipitate with water containing a little ammonium nitrate prevents the formation of colloidal lead molybdate, which would pass through the filter paper. (Use about 2 g. of nitrate per 100 ml.)

The pulp used is paper pulp made by breaking up ashless filter paper and agitating it thoroughly with hot water in a flask. W. W. Scott preferred omitting the pulp and using a fine-grained ashless filter paper; the washing of the precipitate being conducted with wash water containing ammonium nitrate. A filter crucible may be used in place of a paper filter.

DETERMINATION OF LEAD AS THE CHROMATE, $PbCrO_4$

This method is applicable to a large class of materials and is of special value in precipitation of lead from an acetic acid solution, the method depending upon the insolubility of lead chromate in weak acetic acid.

Procedure.—The solution of the sample, precipitation of the lead as the sulfate and extraction of lead with ammonium acetate have been given in detail.

The filtrate, containing all the lead in solution as the acetate, is acidified slightly with acetic acid and heated to boiling. Lead is precipitated by addition of potassium dichromate solution in excess (10 ml. of 5% $K_2Cr_2O_7$ solution are generally sufficient). The solution is boiled until the yellow precipitate turns to a shade of orange or red.[8] The precipitate is allowed to settle until the supernatant solution is clear. (This should appear yellow with the excess of dichromate reagent.) The $PbCrO_4$ is filtered onto an asbestos mat in a tared filter crucible, washed with water, dried in an oven at about 110° C. and the cooled compound weighed as $PbCrO_4$.

$$PbCrO_4 \times 0.6411^8 = Pb.$$

NOTES.—Impurities, such as iron, copper, cadmium, etc., in the acetate solution of lead seriously interfere in the chromate precipitation. These should be leached out with water containing a little sulfuric acid before extracting the lead sulfate with ammonium acetate. See remarks under section on Traces of Lead.

If a standard solution of potassium dichromate is used in the precipitation of lead the excess of the reagent, upon filtering off the precipitate, may be titrated and the lead determined volumetrically. A known amount of dichromate solution (added from a burette) sufficient to precipitate all the lead and about one-third of the volume in excess is added to the hot solution. After boiling about two minutes the precipitate is filtered off quickly and washed several times with hot water. The filtrate, or an aliquot part of it, is made acid with 5 ml. of concentrated sulfuric acid and titrated with standard ferrous sulfate at about 60° C., using potassium ferricyanide as an outside indicator; the end-point is a blue color produced by the slight excess of the ferrous salt reacting with the indicator. The excess of dichromate may be determined by adding 3 to 4 grams of solid potassium iodide, KI, to the solution diluted to about 500 ml. with water to which 15 ml. of concentrated sulfuric acid have been added. The liberated iodine is titrated with standard thiosulfate, with starch solution indicator. Bi, Sb, Ba, Sr and Ca interfere slightly.

One ml. N/10 $K_2Cr_2O_7$ = 0.01036 gram Pb. One ml. N/5 $K_2Cr_2O_7$ = 0.02072 gram Pb.

ELECTROLYTIC DETERMINATION OF LEAD AS THE PEROXIDE, PbO_2

An electric current passed through a solution of lead containing sufficient free nitric acid will deposit all the lead on the anode as lead peroxide. The method is excellent for analysis of lead alloys. The following substances interfere: Bi, Sn, Sb, Ag, Mn will contaminate the PbO_2 precipitate; Cl, Hg, As, Te, Se, P prevent complete deposition.

[8] The yellow precipitate gives high results, since it is difficult to wash. The crystalline orange or red compound may be quickly filtered and washed. The A. S. T. M. recommends the factor 0.6375 when the lead has been separated as the chloride.

If Bi is present add 2 g. of citric acid dissolved in a little hot water before filtering off the $PbCrO_4$.

Procedure.—The sample containing not over 0.1 gram lead is brought into solution by heating with dilute nitric acid, 1 : 1. The solution is washed into a large platinum dish with unpolished inner surface. Twenty to 25 ml. of concentrated nitric acid (sp. gr. 1.42) are added and the solution diluted to about 150 ml.

The sample is electrolyzed in the cold with 0.5 to 1 ampere current and 2 to 2.5 volts, the platinum dish forming the anode of the circuit, a spiral platinum wire or a platinum crucible dipped into the solution being the cathode. Three hours are generally sufficient for the deposition of the Pb. Overnight is advisable, a current of 0.05 ampere being used.

A rapid deposition of the lead may be obtained by heating the solution to 60 to 65° C. and electrolyzing with a current = 1.5 to 1.7 amperes per 100 sq. cm., the E.M.F. varying within wide limits. Stirring the solution with a rotating cathode aids in the rapid deposition of the PbO_2.

To ascertain whether all the lead has been removed from the solution, more water is added so as to cover a fresh portion of the dish with water. The electrolysis is complete if no fresh deposition of the peroxide takes place after half an hour.

The solution is siphoned off while more water is being added until the acid is removed, the current is then broken, the dish emptied of water and the deposits dried at 220° C. and weighed as PbO_2.

$$PbO_2 \times 0.8643 = Pb. \text{ (Empirical Factor)}$$

Note.—The deposit of lead peroxide may be removed by dissolving off with warm dilute nitric acid (1 : 3) and a little H_2O_2.

For volumetric estimation of the peroxide PbO_2 see page 524.

VOLUMETRIC METHODS

VOLUMETRIC FERROCYANIDE METHOD FOR THE DETERMINATION OF LEAD

Although the gravimetric methods for the determination of lead are considered the more accurate, yet the volumetric procedures may be frequently used with advantage. The ferrocyanide method has been pronounced by Irving C. Bull [9] to be the best of the procedures in common use, the results being accurate.

Procedure.—Lead sulfate is obtained according to the method outlined under Preparation and Solution of the Sample. The lead sulfate is transferred to a small beaker and gently boiled with 10 to 15 ml. of a saturated solution of

[9] Chem. News, 87, 53, 1903.

ammonium carbonate, the liquid having been added cold and brought up to boiling. After cooling, the precipitate is filtered on the original filter paper from which the lead sulfate was removed. The lead carbonate is washed free of alkali with cold water. The filter with the precipitate is dropped into a flask containing a hot mixture of 5 ml. of glacial acetic acid with 25 ml. of water. The lead carbonate is decomposed by boiling and the solution diluted to 100 ml.

Titration.—The sample warmed to 60° C. is titrated with a standard solution of potassium ferrocyanide, using a saturated solution of uranium acetate, as an outside indicator. The excess of ferrocyanide produces a brown color with the uranium acetate drop on the tile.

Free ammonia must be absent, as it reacts with uranium acetate and gives low results. NH_4OH precipitates reddish brown, gelatinous uranous hydroxide, $U(OH)_4$.

The bulk of solution to be titrated should be as near as possible to 100 ml., including 5 ml. of glacial acetic acid.

A 1% potassium ferrocyanide solution is used in the titration. This reagent is standardized against a known amount of lead in solution as an acetate.

A correction of 0.8 ml. is generally necessary on account of the indicator. This is determined by a blank titration.

Antimony, bismuth, barium, strontium and calcium interfere only to a very slight extent, the error being negligible.

THE PERMANGANATE METHOD FOR LEAD[10]

The following method for the determination of lead in ores has proved very satisfactory in the great majority of cases. It depends upon the separation of the lead as sulfate, the conversion of the sulfate to carbonate, the solution of the carbonate in acetic acid, followed by the precipitation of the lead as oxalate. The lead oxalate is then decomposed in dilute sulfuric acid and the separated oxalic acid titrated with standard permanganate.

Ordinary constituents of lead ores do not interfere, with the exception of lime. As high as 10% of CaO in an ore, however, is without effect. Barium interferes only by forming a combination with lead that resists the reactions, with consequent low results. The remedy is easy and is described below.

Procedure.—Decompose 0.5 gram of the ore in a 250-ml., pear-shaped flask, such as is commonly called a "copper-flask." The treatment may usually be a very gentle boiling with 10 ml. of hydrochloric acid for a short time, then adding 5 ml. of nitric acid and continuing the gentle boiling until decomposition is complete. Now add 6 ml. of sulfuric acid and boil over a free flame to strong fumes. Allow to cool.

Add 100 ml. of cold water and 5 ml. of sulfuric acid and heat to boiling. Remove from the heat, add 10 ml. of alcohol (cautiously) and cool under the tap.

Fold a 9-cm. filter with particular care to creasing the fold that will come next to the precipitate as thin as possible, so it will lie flat and not easily allow material to get under the edge. Filter the mixture through this. Return the first portions of the filtrate if not clear. Wash 6 times with cold water containing 10% of alcohol. Any trace of lead sulfate remaining in the flask will be recovered subsequently.

[10] By Albert H. Low.

With a jet of hot water, using as little as possible, rinse the precipitate from the filter, through a short funnel, back into the flask. (In the known or assumed presence of barium, interpolate the following short procedure: Add 10 ml. of hydrochloric acid and boil over a free flame almost to dryness. Allow to cool, add 20 ml. of water and a few drops of ammonia, sufficient to neutralize the acid.) Place the flask again under the original funnel and pour through the filter 10 ml. of a cold saturated solution of ammonium carbonate. Remove the flask and heat the contents just to boiling, then cool completely under the tap. Pour the cold mixture through the original filter. Wash out the flask well with cold water, pouring through the filter, and then wash filter and precipitate 10 times with cold water containing about 5% of the ammonium carbonate solution. Reject the filtrate.

Again using a jet of hot water, wash the precipitate from the filter into a small beaker. Add 5–6 ml. of glacial acetic acid and heat to boiling. Replace the flask under the funnel and pour the hot acid mixture through the filter. Wash out the beaker with hot water and then wash the filter 10 times with hot water slightly acidulated with acetic acid. (Small amounts of lead carbonate may be dissolved directly upon the filter, without previous transference to a beaker.)

Add to the filtrate 10 ml. of a cold saturated solution of oxalic acid, heat to boiling and then cool completely under the tap. Be particular to get as cold as possible. Now filter the lead oxalate through a 9-cm. filter. Using cold water, wash out the flask thoroughly and then wash filter and precipitate 10 times.

Place about 25 ml. of cold water in the flask, add 5–6 ml. of sulfuric acid and then about 100 ml. of hot water. Drop the filter and precipitate into this. Wipe out any lead oxalate adhering in the funnel with a small piece of dry filter paper and drop into the flask. Heat the acid mixture nearly to boiling and then titrate it with standard potassium permanganate solution to a faint pink tinge. Calculate the result from the known lead value of the permanganate.

The permanganate commonly used for iron titrations will serve, although rather strong for lead. Theoretically, 1.857 times the iron factor will give the lead factor. Owing to slight losses of lead an empirical factor must be used. This is 1.879 times the iron factor. Based on this factor and on 0.5 gram of ore taken for assay, 1 ml. of a permanganate solution containing 1.544 grams per liter will equal 1% lead. It may be standardized directly on lead as follows: Convert about 0.250 gram of pure lead foil to sulfate by boiling with 6 ml. of sulfuric acid. Continue according to the above entire process. Finally, divide the percentage value of the lead taken by the ml. of permanganate required, to obtain the percentage value of 1 ml. in lead. A comparison of this figure with the iron value of the permanganate may be made, to check the conversion factor given above. The personal equation may cause a slight difference.

NOTES.—Metallic lead is converted to lead sulfate by boiling with strong sulfuric acid. The reaction takes place with the hot concentrated acid, the metal changing to the white lead sulfate solid, soluble in large excess of sulfuric acid; this is unnecessary, as decomposition is complete with the amount stated.

Conversion of lead sulfate to carbonate before changing to acetate appears at first thought to be an unnecessary step, but experience has shown that a direct conversion of sulfate to acetate by dissolving in ammonium acetate leaves sufficient sulfate in the solution to cause low results, as much as 10% of lead apparently escaping subsequent conversion to oxalate. In the procedure for converting the lead to carbonate any small amount of lead sulfate remaining does no harm. It frequently occurs that

the carbonate formed does not completely dissolve in acetic acid. If a cloudy solution is obtained, a few drops of ammonia will furnish enough ammonium acetate to dissolve the small amount of sulfate remaining. The precipitation of lead oxalate is not interfered with by the ammonium salt present, a large amount of which, however, should be avoided. Ammonium oxalate may be added in place of oxalic acid.

VOLUMETRIC DETERMINATION OF LEAD BY THE MOLYBDATE METHOD

Lead is precipitated from an acetic acid solution by a standard solution of ammonium molybdate, the termination of the reaction being recognized by the yellow color produced by the excess of reagent when a drop of the mixture comes in contact with a drop of tannin solution, used as an outside indicator. The method is rapid, but is not as accurate as the chromate-iodide method.

Reagents. *Ammonium Molybdate.*—4.26 grams of the salt are dissolved in water and diluted to 1000 ml. On a half gram sample basis 1 ml. of the reagent is equivalent to about 1% lead.

Standardization.—Dissolve 0.2 g. of pure lead foil in 5 ml. of conc. sulfuric acid by boiling gently in a 250-ml. pear-shaped flask. When the lead has been converted to sulfate, dilute (on cooling) with water and filter off the $PbSO_4$. Now follow the details of the procedure given below, after isolating the lead as sulfate. Note the ml. of molybdate reagent required and divide this into 0.2 to get the equivalent value in terms of lead per ml. of reagent. One ml. should be equivalent, approximately, to 0.005 g. Pb.

Tannin Indicator.—0.1 g. tannic acid per 20 ml. water. The reagent should be prepared fresh for each day's analysis.

Procedure. *Decomposition.*—Follow the usual procedure recommended for decomposing lead ores, using HCl, HNO_3 and finally H_2SO_4. Evaporate to strong sulfuric fumes, and take up with water. Filter off the lead sulfate and wash with a 10% sulfuric acid solution, to remove sulfates of the metals, and finally with water containing a little alcohol, remembering that $PbSO_4$ is slightly soluble in water.

The lead sulfate is now brought into solution as lead acetate by extraction with ammonium acetate slightly acidified with acetic acid. (Use a strong solution of the reagent.) In absence of calcium and barium, the writer prefers to convert the lead sulfate to carbonate by boiling with ammonium carbonate solution, according to the permanganate method for lead (p. 509), and then to the acetate by dissolving the lead carbonate in dilute acetic acid. Thus sulfates are eliminated. The addition of a few drops of ammonia to the acetic acid solution insures the solubility of the lead. ($PbSO_4$ may be present in small amount and does not readily dissolve in acetic acid.) The results are more concordant in absence of sulfate. The acetate solution of lead is now titrated with the standard molybdate solution.

Titration.—The solution is divided into two portions, one being kept in reserve. To one is added the standard solution of ammonium molybdate, from a burette, until a drop of the titrated solution, brought in contact with a drop of tannin indicator, on a white tile, or paraffined surface, gives a brown or yellow color. The reserve solution is now added in portions, the titration being continued, until the last portion has been used and the brown color obtained. This precaution avoids over-running the end-point.

THE CHROMATE-IODIDE METHOD FOR THE VOLUMETRIC DETERMINATION OF LEAD

The method depends upon the action of chromates on potassium iodide with a resulting liberation of an amount of free iodine in direct ratio to the chromate present, which in turn is a measure of the amount of lead isolated as lead chromate. The liberated iodine is determined by titration with a standard solution of thiosulfate.

Solutions Required. *Ammonium Acetate Extraction Solution.*—A saturated solution of ammonium acetate, filtered to remove foreign matter if present, is diluted with twice its volume of distilled water and 30 ml. of 80% acetic acid is added per liter of solution.

Hydrochloric Acid Mixture.—To a liter of saturated salt solution, filtered if necessary, are added 150 ml. of distilled water and 100 ml. of concentrated hydrochloric acid.

Potassium Dichromate.—Saturated solution, filtered if not clear.

Starch Solution.

Procedure. 1. *Solution of the Sample.*—Half a gram of the finely divided ore (if the factor weight 0.6907 g. is taken, 1 ml. N/10 reagent in final titration is equivalent to about 1% Pb) is dissolved in a beaker or a flask (Low's type) by adding 20 ml. of conc. hydrochloric acid and heating gently until the action subsides. If the decomposition is incomplete, about 5 ml. of nitric acid are added and the heating continued.

2. About 5 ml. of sulfuric acid are added and the solution evaporated to strong fumes. After cooling, about 50 ml. of water are added and the solution is boiled to dissolve the soluble salts. If the ore is low grade, 5–10 ml. of ethyl alcohol are now added, the precipitate is allowed to settle and then washed by decantation three or four times with 1 : 15 sulfuric acid (i.e., about 10% solution), and finally transferred to the filter with the dilute acid and washed once with pure cold water.

3. By means of a fine jet from a wash bottle filled with ammonium acetate extraction reagent, heated to near boiling, the precipitate is transferred to the beaker or flask in which the precipitation was made. This may be done by carefully spreading out the filter in the funnel or by breaking the filter and washing the paper free of the lead sulfate with a fine stream of the reagent. If the precipitate does not go into solution, more of the acetate is added and heat gently applied until it dissolves. The solution is now diluted to 150 ml., heated to boiling and 10 ml. of the saturated dichromate solution added and the boiling continued ten minutes. The yellow color of the lead chromate precipitate changes to red. This is important to obtain a precipitate of definite composition.

4. The precipitate is filtered, the containing vessel washed out with hot dilute ammonium acetate wash solution (50 ml. of the extraction solution diluted to 1000 ml.) and the precipitate washed ten times with the reagent.

5. The original beaker or flask is now placed under the funnel and the lead chromate is dissolved on the filter by adding cold dilute hydrochloric acid mixture, stirring up the precipitate with a jet of the reagent, adding the acid until all the chromate has dissolved and the color has been completely removed from the filter. At least 50 ml. of the reagent should be used.

At this stage either of the following methods may be followed; both procedures give good results. The second method (J. Ind. Eng. Chem., 17, 678, 1925) is less expensive.

A. Reduction by Iodide

For low grade ores the entire solution is taken and treated with potassium iodide solution; in case of high grade ores, about half the solution is set aside in reserve, and upon completing the titration of the first portion, the reserve is added and the titration completed. This precaution is taken because a loss of iodine is apt to occur if much iodine is liberated at one time, free iodine being apt to escape as vapor from the easily saturated solution. (The solution is a poor solvent of iodine.) To the solution are added 5 ml. of 25% potassium iodide and the liberated iodine is titrated with N/10 sodium thiosulphate until the iodine color begins to fade; starch solution is now added in sufficient quantity to produce a distinct blue color and the titration continued until the blue color changes to pale green.

A background of white assists in recognition of the end-point. A sheet of white paper placed under the beaker will do, if the base of the stand is not already white.

Standardization of the Thiosulfate.—This is best standardized against metallic lead. 0.6907 gram of pure lead should require 100 ml. of N/10 thiosulfate. 0.2 gram of lead is taken or a fraction of the factor weight (0.6907). The lead foil is dissolved in 5 ml. of sulfuric acid by bringing to vigorous boiling; upon cooling the residue is taken up with water and treated exactly according to the method outlined in steps 2–6 of the regular procedure. One ml. of N/10 thiosulfate is equivalent approximately to 0.0069 gram of lead.

Notes.—If barium is present in the sample, the residue left from the acetate extraction may contain lead. This is treated with about 10 ml. of strong hydrochloric acid, evaporated to dryness, 25 ml. of the acetate reagent added, the mixture boiled, filtered and the residue washed. The filtrate contains the lead that remained with the residue.

In considering the reactions that take place it must be remembered that it is the combined chromate radical that is responsible for the liberated iodine. The equation represents what takes place:

$$2PbCrO_4+6KI+16HCl=2PbCl_2+2CrCl_3+6KCl+8H_2O+3I_2.$$

It is evident that Pb is equivalent to 3I. Therefore a normal equivalent of Pb is $\frac{1}{3}$ of its atomic weight, 207.21 divided by 3 = 69.07, hence 1 ml. of a N/10 solution will titrate iodine equivalent to .006907 g. Pb.

Since Fe equivalent is 55.84, Fe to Pb = 69.07 divided by 55.84 = 1.237, factor of iron to lead.

Example in Standardization of Sodium Thiosulfate.—If 0.2035 g. of lead required 30.05 ml. of thiosulfate solution, then 1 ml. would be equivalent to 0.00677 g. lead.

B. Reduction by Ferrous Sulfate

With experience the results are excellent. In the hands of the inexperienced analyst low results are obtained due to loss of $PbSO_4$ during the washing, incomplete extraction of the sulfate with acetate, loss of chromate and incomplete solution of $PbCrO_4$ before the final steps of titration.

Reagents.—**Ferrous Solution.**—0.1 N. 39.3 g. ferrous ammonium sulfate hexahydrate per liter.

Standardize against 0.1 N. potassium dichromate.

Potassium Dichromate.—0.1 N. 4.903 grams per liter.

Phosphoric-Sulfuric Acid Mixture.—One volume 85% H_3PO_4 with 1 volume H_2SO_4 (1.84).

Diphenylamine Indicator.—One gram dissolved in 100 ml. H_2SO_4 (1.84).

The chromate solution is diluted to about 100 ml, 10 ml. of phosphoric-sulfuric acid mixture are added and 4–5 drops of diphenylamine indicator. The standard ferrous sulfate reagent is now run in until the yellow color changes to green. The excess of ferrous sulfate is oxidized by back titration with standard dichromate reagent until the green color changes to a deep blue. The difference between the two titrations (the ml. must be converted to a common basis of 0.1 N by multiplying by the factors of the reagents before subtracting the $K_2Cr_2O_7$ titration from the $FeSO_4$ titration) is due to the ferrous sulfate oxidized by the chromate.

One ml. of 0.1 N. ferrous sulfate solution required by the chromate is equivalent to 0.006907 g. Pb.

NOTES.—If much HCl is present the blue color will not be obtained. Addition of 1 g. ammonium acetate per ml. HCl present will prevent this difficulty. If the end-point is a dirty green in place of blue add the solid acetate until a blue color develops. Add additional standard ferrous sulfate until a green color is obtained and back titrate with dichromate to a blue color. Note the total ferrous and dichromate reagents used.

DETERMINATION OF SMALL AMOUNTS OF LEAD

The determination of minute quantities of lead is required in baking powders canned goods and like products in which small amounts of lead are objectionable. Traces of lead ranging from 5 to 100 parts per million (0.0005 to 0.01% Pb) are best determined colorimetrically on 0.5 to 1 gram samples; larger amounts of lead should be determined gravimetrically.

GRAVIMETRIC METHODS FOR DETERMINING TRACES OF LEAD

The determination of extremely small amounts of lead cannot be accomplished by the usual methods of precipitation, as the lead compounds remain in solution in a colloidal state. The addition, however, of certain substances, which form amorphous precipitates with the reagents used for throwing out lead causes the removal of lead from the solution by occlusion. For example,

adding a sufficient quantity of a soluble salt of mercury, copper, or arsenic to a solution containing a trace of lead, and then saturating the solution with H_2S, will cause the complete removal of lead from the solution. Iron and alumina thrown out of the solution as hydroxides will carry down small amounts of lead, and completely remove it from the solution, if they are present in sufficient quantity. Lead may be extracted from finely pulverized substances by means of hot ammonium acetate and precipitated from the extract as lead sulfide. Advantage may be taken of these facts in determining traces of lead in presence of large amounts of other substances.

Amount of the Sample.—It is advisable to have the final isolated lead compound over 0.01 gram in weight, hence, in a sample containing 10 parts of lead per million, 800 to 1000 grams of the material should be taken, since a kilogram of the material would contain 0.01 gram, Pb or 0.0156 gram $PbCrO_4$, or 0.0146 gram $PbSO_4$, or 0.0177 gram $PbMoO_4$. Large samples should be divided into several portions of 100 to 250 grams each, the lead isolated in each, and the final extracts, containing the lead, combined. For the given amount of occluding agent, stated in the procedure, the treated portion should contain not over 0.01 gram lead.

EXTRACTION OF LEAD WITH AMMONIUM ACETATE AND SUBSEQUENT PRECIPITATION

It is frequently desirable to extract the lead from the mass of material and precipitate it from the liquor thus obtained. The procedure worked out by the writer is applicable to determining traces of lead in aluminum salts, but with modifications may be applied to a wide range of substances.

Extraction of Lead.—The desired weight of finely powdered substance, in 100-gram portions, is placed in 6-inch porcelain casseroles (1000 ml. capacity). To each portion are added, with vigorous stirring, 500 ml. of *lead-free*, boiling hot ammonium acetate solution (33%).[11] The reaction is apt to be energetic, so that care must be exercised to avoid boiling over. The residue from aluminum salts is crystalline and may be separated from the extract very readily by filtering through two filter papers in a large Büchner funnel and applying suction.[12] The residue is tamped down to squeeze out the adhering extract and washed with 100 ml. more of hot ammonium acetate followed by 100 to 200 ml. of hot water, again tamped down and sucked as dry as possible. The lead extracts are now combined and lead precipitated as sulfide.

Precipitation of Small Amounts of Lead.—To the solution containing lead are added 2–3 ml. of a 10% copper sulfate or cadmium sulfate reagent. Hydrogen sulfide is passed into the liquor until it is saturated. The copper or cadmium sulfide assists the settling of lead sulfide. Gently warming on the steam

[11] The reagent is made by dissolving one part of lead-free ammonium acetate in two parts of distilled water. The purity of the reagent should be tested. The reagent must be boiling, when added, to obtain best results. Experiments have shown that considerable alumina and iron dissolve if the proportion of the reagent falls much below 5 ml. of 33% acetate per gram of sample. With twice this amount of reagent the extract is free from iron and alumina. Small amounts of alumina and iron, however, do not interfere in the lead determination.

[12] 200 to 300 grams of material may be handled in a 6-inch Büchner funnel.

bath for half an hour coagulates the precipitate and facilitates settling. The liquor is decanted through a double filter in a small Büchner funnel and the residue washed onto the filter with water saturated with H_2S gas.

The precipitate is washed several times with ammonium sulfide to remove sulfides of the arsenic group and the residue then dissolved in a hot mixture of hydrochloric and nitric acids (1 part HCl, 5 parts HNO_3 and 15 parts H_2O). Ten ml. of conc. sulfuric acid are added to the solution, and the mixture is evaporated to SO_3 fumes *but not to dryness*. The residue is taken up with 100–125 ml. of water containing 2 ml. of sulfuric acid and boiled to dissolve the soluble salts of iron, alumina, copper, etc. After cooling, one-third the volume of 95% alcohol is added (30–40 ml.), the lead sulfate allowed to settle for an hour or more, then filtered and washed several times with 30% alcohol. The residue is extracted with hot ammonium acetate and lead chromate precipitated from the filtrate,[13] made slightly acid with acetic acid, by adding 10 ml. of potassium dichromate reagent and boiling, filtering, washing, drying and weighing, according to the standard procedure. (Page 507.)

$$PbCrO_4 \times 0.6411 = Pb.$$

PRECIPITATION OF LEAD BY OCCLUSION WITH IRON HYDROXIDE

Wilkie found [14] that ferric hydroxide has the property of occluding lead, five parts of $Fe(OH)_3$ removing one part of lead from solution. Advantage is taken of this property of iron hydroxide in precipitating small amounts of lead.[15]

Procedure.—The required amount of material is weighed out in 50-gram lots and brushed into large beakers. If the material contains organic matter, it is treated with 200-ml. portions of concentrated hydrochloric acid, the mixture heated just below the boiling-point of HCl solution, and potassium chlorate added, a few crystals at a time, until the organic matter is decomposed (hood). If the material dissolves in water, the water solution is treated with 5 ml. of concentrated hydrochloric acid and a few crystals of potassium chlorate and the liquor boiled.

Addition of Ferric Iron.—If sufficient iron is not already present, ferric chloride is added in such quantity that the iron content of the sample will be from twenty to fifty times that of the lead (larger amounts of iron will do no harm) present in the solution. Five to 10 ml. of concentrated nitric acid are added and the sample boiled for ten to fifteen minutes.

Precipitation of Iron and Lead.—Ammonium hydroxide is now added to precipitate all of the ferric hydroxide. This highly absorbing precipitate adsorbs the finely divided or colloidal lead compound carrying it out of solution completely. The solution is filtered hot through fast filters, threefold. The filtering must be rapid and the liquid kept hot to prevent clogging of the filters.

[13] Should lead chromate fail to precipitate, the solution should be treated with H_2S to complete saturation, the sulfide collected on a filter, then dissolved in acid and the procedure described above repeated. If the solution still remains clear, the absence of lead is confirmed.

[14] J. M. Wilkie, Chem. News, 99, 311, 1909.

[15] Occlusion of lead by zinc sulfide, precipitated by H_2S from a formic acid solution, is suggested; iron and alumina would not interfere.

Separation of Lead from Iron.—The precipitate is dissolved in hot hydrochloric acid (free from lead). The solutions are combined, if several portions of the sample are taken. Concentrated sulfuric acid is added and the sample evaporated to small volume and heated until the white sulfuric acid fumes appear. The usual procedure is now followed for separation of the lead sulfate, acetate extraction of lead and final precipitation of lead chromate.

$$PbCrO_4 \times 0.6411 = Pb.$$

NOTE.—In place of using alcohol to decrease the solubility of lead sulfate, many prefer to add sulfuric acid so that the acidity of the solution will be 2–10% free H_2SO_4.

MODIFICATION OF SEEKER-CLAYTON METHOD FOR TRACES OF LEAD IN BAKING POWDER

One hundred grams of baking powder are treated with 25 ml. of water followed by 75 ml. of conc. hydrochloric acid added in small portions to avoid excess frothing. The mixture is heated until the starch has decomposed (iodine test gives blue color with starch), the solution becoming clear and turning yellow. The free acid is neutralized with ammonium hydroxide and when the solution is cold, 400 ml. of lead-free ammonium citrate, saturated with H_2S, are added. Additional H_2S is passed into the slightly alkaline solution, the sulfides of iron and lead allowed to settle, the clear supernatant liquor decanted off, the sulfides collected on a filter and washed. The precipitate is dissolved in nitric acid, lead separated as a sulfate, extracted with acetate and precipitated as dichromate according to the procedure recommended under the acetate extraction.

COLORIMETRIC ESTIMATION OF SMALL AMOUNTS OF LEAD

SULFIDE METHOD

Introduction.—Estimation of small amounts of lead by the intensity of the brown coloration produced by the sulfide in colloidal solution was first proposed by Pelouze. The procedure was modified by Warington and by Wilkie to overcome the color produced by accompanying impurities, among these, iron, which is almost invariably associated with lead. The method is useful in determining traces of lead in drinking water, in food products, baking powders, canned goods, phosphates, alums, acids such as sulfuric, hydrochloric, citric, tartaric and the like. By this procedure on a gram sample one part of lead per million may be detected and as high as 50 parts may be estimated. For larger

amounts of lead, a smaller sample must be taken. Nickel, arsenic, antimony, silver, zinc, tin, iron, and alumina, present in amounts such as commonly occur in these materials, do not interfere.

In order to obtain accurate results it is necessary to have the solutions under comparison possess the same general character. "It must be remembered that the tint depends to a large extent on the size of the colloidal particles of lead, which in turn depend upon the nature of the salts in the solution and upon the way that the solution has been prepared." Vigorous agitation, salts of the alkalies and alkaline earths tend to coagulate the colloidal sulfide.

Reagents Required. Standard Lead Solution.—A convenient solution may be made by dissolving 0.1831 gram of lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ in 100 ml. of water, clearing any cloudiness with a few drops of acetic acid and diluting to 1000 ml. If 10 ml. of this solution is diluted to 1000 ml. each ml. will contain an equivalent of 0.000001 gram Pb.

Harcourt suggests a permanent standard made by mixing ferric, copper and cobalt salts. For example 12 grams of $FeCl_3$ together with 8 grams of $CuCl_2$ and 4 grams of $Co(NO_3)_2$ are dissolved in water, 400 ml. of hydrochloric acid added and the solution diluted to 4000 ml. One hundred and fifty ml. of this solution, together with 115 ml. of hydrochloric acid (1 : 2), diluted to 2000 ml. will give a shade comparable to that produced by the standard lead solution above, when treated with the sulfide reagent. The exact value per ml. may be obtained by comparison with the lead standard.

Alkaline Tartrate Solution.—Twenty-five grams of C.P. sodium potassium tartrate, $NaKC_4H_4O_6 \cdot 4H_2O$, is dissolved in 50 ml. of water. A little ammonia is added and then sodium sulfide solution. After settling some time the reagent is filtered. The filtrate is acidified with hydrochloric acid, boiled free of H_2S and again made ammoniacal and diluted to 100 ml.

Ammonium Citrate Solution.—Ammonium citrate solution is prepared in the same way as the tartrate solution above, 25 grams of the salt being dissolved in 50 ml. of water.

Potassium Cyanide.—A 10% solution is made from the lead-free salt.

Sodium Sulfide.—A 10% solution, made from colorless crystals. Sodium sulfide may be made by saturating a strong solution of sodium hydroxide with hydrogen sulfide gas, and then adding an equal volume of the sodium hydroxide. The solution is diluted to required volume, allowed to stand several days, and filtered.

Sodium metabisulfite.—The solid salt, $Na_2S_2O_5$.

Apparatus.—The color comparison may be made in Nessler tubes, or in a colorimeter. The Campbell and Hurley modification of the Kennicott-Sargent colorimeter is excellent for this purpose,[16] Fig. 59. The colorimeter is simple in construction and operation.

The tubes for holding the solutions to be compared are those of one of the well-known colorimeters, in which the unknown solution is placed in the left hand tube while the color is matched by raising or lowering the level of a standard solution in the right-hand tube by means of a glass plunger working in an attached reservoir.

The accompanying diagram shows the essential features of construction of the colorimeter employed in the tests described below. The unknown solution

[16] J. Am. Chem. Soc., 33, 1112, 1911.

is placed in the left-hand tube *A*, which is 19 cm. long, 3 cm. in diameter, and graduated for 15 cm. The standard solution is placed in the right-hand tube *B*, which is the same size as *A*, the graduated portion being divided into 100 divisions of 1.5 mm. each. The tube *B* is permanently connected by a glass tube with the reservoir *C* in which the glass plunger *D* works, so that the level of the liquid in *B* can be readily controlled by raising or lowering the plunger. As the tube *B* and reservoir *C* are made in one piece, the liquid used for the standard solution comes in contact with glass only, thus preventing any possibility of chemical change due to contact with the container. The plunger is pro-

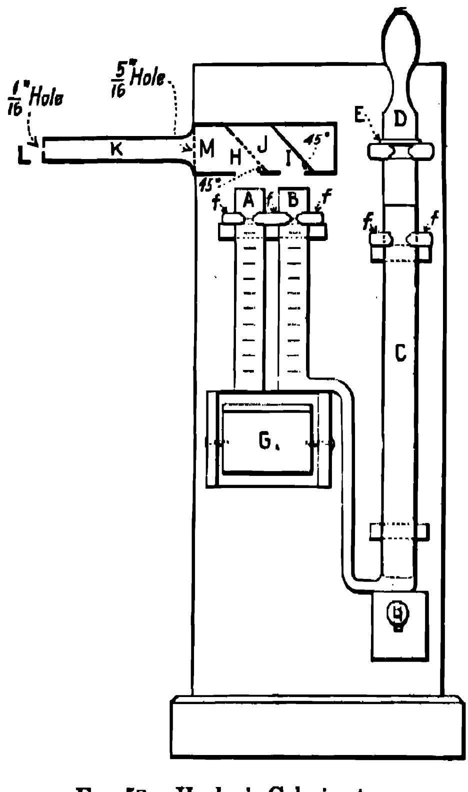


FIG. 59.—Hurley's Colorimeter.

vided with a rubber collar *E*, so placed as to prevent the plunger from accidentally striking and breaking the bottom of the reservoir. The tubes *A* and *B*, with the connecting reservoir, rest on wooden supports, the one under *A* and *B* being provided with holes for the passage of the light, and are held in position by spring clips *f f*. This arrangement allows the glass parts to be readily removed for cleaning and filling. The light for illuminating the solution is reflected upward through the tubes *A* and *B* by means of the adjustable mirror *G*. The best results are obtained by facing the colorimeter toward a north window in order to get reflected skylight through the tubes, care being taken to avoid light reflected from adjacent objects. The black wooden back of the colorimeter

serves the double purpose of a support for the parts of the instrument and of a screen, as it is interposed between the color tubes and the source of light.

The light, passing upward through the tubes *A* and *B*, impinges on the two mirrors *H* and *I* cemented to brass plates sliding in grooves cut at an angle of 45° in the sides of the wooden box *J*. This box is supplied with a loosely-fitting cover, thus allowing easy access for the purpose of removing and cleaning the mirrors. The mirror *H* is cut vertically and cemented in such a position as to reflect one-half of the circular field of light coming through the tube *A*. The light passing upward through *B* is reflected horizontally by the mirror *I*, through a hole in the brass plate supporting the mirror *H*. One-half of the circular field of light from the tube *B* is cut off by the mirror *H*, the vertical edge of which acts as a dividing line between the two halves of the circular field. The image of one-half of the tube *B* is then observed in juxtaposition to the opposite half of the image of the tube *A*.

The juxtaposed images are observed through a tube *K*, 2.5 cm. in diameter and 16 cm. long, lined with black felt and provided with an eye-piece having a hole 1.5 mm. in diameter. At the point *M* in the tube *K* is placed a diaphragm having an aperture 8 mm. in diameter. All parts inside the box *J* except the mirrors are painted black so that no light except that coming through the tubes *A* and *B* passes through the tube *K*. By having the apertures in the eye-piece and diaphragm properly proportioned only the image of the bottoms of the tubes *A* and *B* can be seen, thus preventing interference of light reflected from the vertical sides of the tubes *A* and *B*.

A person looking through the eye-piece observes a single circular field divided vertically by an almost imperceptible line when the two solutions are of the same intensity. By manipulating the plunger *D*, the level of the liquid in *B* can be easily raised or lowered, thus causing the right half of the image to assume a darker or lighter shade at will. In matching colors with an ascending column in *B*, that is, gradually deepening the color of the right half of the field, the usual tendency is to stop a little below the true reading while in a comparison with a descending column the opposite is the case.

Procedure.—If lead is between 10 to 50 parts per million a 1-gram sample is taken. If it is above or below these extremes the amount of sample is regulated accordingly. In materials containing organic matter it is not advisable to take more than a 1-gram sample.

Substances containing organic matter, such as starch in baking powder, should be decomposed by fusion with sodium peroxide, or with sodium or potassium sulfate containing a few drops of sulfuric acid. A Kjeldahl digestion with concentrated sulfuric acid and potassium bisulfate may occasionally be advisable. Sulfuric acid discolored by organic matter should be mixed with 4 to 5 grams of potassium bisulfate, taken to fumes and then diluted with water. The material may be extracted with ammonium acetate and lead determined in the extract. See notes.

To the solution containing the sample are added 10 ml. of tartrate solution (or 20 ml. of citrate solution with phosphates of lime, etc.), 10 ml. of hydrochloric acid and the mixture brought to boiling. Small amounts of ferric iron are now reduced by adding 0.5 gram sodium metabisulfite. Sufficient ammonium hydroxide is added to neutralize the free acid and 5 ml. in excess; then 3 ml. potassium cyanide (to repress any copper color that may be present to

reduce higher oxides), and the mixture heated until the solution becomes colorless. The entire solution or an aliquot portion is placed in the comparison cylinder, and diluted to nearly 100 ml. If the Kennicott-Sargent apparatus is used the standard color solution is forced into the adjacent cylinder, until the color in this cylinder matches the one containing the sample. The number of ml. of the standard is noted. This blank is due to the slight color that the solutions of the samples invariably have. Four drops of the sulfide reagent are added to the sample and this is mixed by means of a plunger, avoiding any more agitation than is absolutely necessary to make the solution homogeneous. After one minute the comparison is again made, the colored standard being forced into the cylinder until its color matches the sample. It is advisable to take several readings with ascending and descending column of standard reagent, taking the average as the true reading.

Calculation.—Suppose the standard = 0.000001 gram Pb per ml., blank = 5 ml., total reading = 22 ml., one gram of sample being taken for analysis. Then 22 − 5 = 17 ml. = 0.0017% Pb or 17 parts per million.

NOTES.—Iron must be completely reduced before adding ammonium hydroxide and potassium cyanide.

Allen's method of reducing iron with sodium metabisulfite is excellent. The salt may be made by passing SO_2 into a saturated solution of sodium carbonate at boiling temperature, until the liquor is just acid to methyl orange. The water evaporated during the treatment is replaced during the action. $Na_2S_2O_5$ separates and may be filtered off and the water removed by centrifuging.

If a separation from iron is desired, the lead may be extracted with ammonium acetate solution. Ten grams of the powdered material are mixed with 75 ml. of a 33% ammonium acetate solution [17] (25 grams of the salt dissolved in 50 ml. H_2O), the reagent being added boiling hot. The mixture is diluted to 500 ml., a portion filtered, and the determination made on an aliquot part of the total, following the directions above.

The following may be present, if their amounts do not exceed the following limits: nickel 0.1%, arsenic 0.2%, zinc 0.2%, antimony 0.05%, copper 0.25%, iron 1.0%, aluminum 10%, tin 1.4%.

DITHIZONE EXTRACTION METHOD-COLORIMETRIC DETERMINATION [18]

Dithizone is a contraction for diphenylthiocarbazone, $C\begin{cases} N{=}N-C_6H_5 \\ {=}S \\ NH-NH-C_6H_5. \end{cases}$

The reagent is capable of detecting 1 part of lead per 20 million parts of solution. Many other metals react with the reagent, but there are only three, Sn^{II}, Bi and Tl^{I} that are extracted with the lead from ammoniacal cyanide solution by a chloroform solution of the reagent. Oxidizing agents destroy the reagent. After extraction and suitable separations, the lead may be determined either by the color of the chloroform extract (brick red), or by other colorimetric

[17] The ammonium acetate should be free from lead.

[18] H. Fischer, Z. angew. Chem., 42, 1025 (1929); Fischer and Leopoldi, Z. angew. Chem., 47, 90 (1934); Winter et al., Ind. Eng. Chem., Anal. Ed. 7, 265 (1935); Willoughby et al., Ind. Eng. Chem., Anal. Ed. 7, 33, 285 (1935); Wayne E. White, ibid., 8, 231 (1936); Garatt, Analyst, 60, 817 (1935); Ellis, Analyst, 61, 178 (1936); Clifford and Wichmann, J. Assoc. Official Agr. Chem., 19, 130 (1936); Methods of Analysis, Assoc. Official Agr. Chem., 4th Ed., pp. 375–389, 1935.

procedures, for example the sulfide colorimetric method. The dithizone coloimetric method applies for 0.2 to 0.0001 mg. of Pb.

Reagents Needed. *Dithizone.*—The commercial reagent may be purified by dissolving about 1 g. of it in 50 ml. of chloroform and extracting with pure or redistilled 1% ammonia solution in successive portions of about 75 ml. each (the reagent is orange colored in ammoniacal solution). The ammoniacal extracts are combined, acidified with HCl, and the reagent is then extracted to $CHCl_3$ used in successive portions of about 20 ml. each. The reagent is recovered by evaporation and drying at not over 50° C. Suitable reagents contain from 1 to 10 mg. dithizone per 100 ml. of chloroform. The solution should be green.

Citric acid.—0.5 g. per ml. (free from lead).

Potassium Cyanide.—10% in redistilled water.

Conc. Ammonia.—Redistilled.

Standard Lead Solution. 1 mg. per ml. in 1% HNO_3.

Test of Reagents.—Add citric acid equal to the maximum amount to be used (10 g.) to an excess of distilled ammonia, so that the pH is greater than 9. Add 10 ml. of 10% KCN solution, and shake in a separatory funnel with dithizone reagent. If the layer of chloroform is more than faintly red, it will be necessary to purify appropriate ammoniacal mixtures by dithizone extraction before using them in a determination. With good redistilled reagents the blank should be small and fairly reproducible.

Apparatus.—Separatory funnels ranging up to 300 ml. capacity are needed. These should be of lead-free glass. Soft glass is generally very unsatisfactory and Pyrex ware is superior. All vessels should be scrupulously clean, the final rinsing to be with freshly distilled water (best from a resistant glass still).

Procedure.—An adequate sample is prepared either by simple solution in appropriate lead free reagents (distilled water or nitric acid), or by dry or wet destruction of organic matter, followed by HNO_3.

After adding from 1 to 10 g. of citric acid depending on the amount of iron, aluminum etc. expected, make the solution ammoniacal with pH between 8.5 and 10 (bluish-green to blue toward a drop of thymol blue), after neutralizing and adding 5 ml. of 10% KCN solution. Extract with successive 20 ml. portions of dithizone reagent. With small expected amounts of lead, a 1 mg. per 100 ml. solution is used, and more concentrated reagents for larger lead content.

Prepare standards from the standard lead solution using the same quantities of all reagents as used in the analysis, and extracting in the same fashion. Use Nessler tubes for the comparison. The color standards are stable enough to last for at least 1 day.

NOTES.—Tin may be removed after the extraction by evaporation, destruction of the organic matter. The metals are extracted from the chloroform with 10% HCl solution, and the tin is volatilized by repeated evaporation to dryness after adding 10 ml. of $HBr-Br_2$ mixture (100 ml. 40% HBr plus 15 ml. bromine, both redistilled). The lead may be redissolved in nitric acid and converted into the dithizone complex.

Bismuth is extracted by dithizone from a solution at pH 2. The acidity is adjusted with the aid of m-cresol purple indicator by adding ammonia or nitric acid as may be necessary. The solution should be of 25–30 ml. volume and should be extracted twice with equal portions of dithizone reagent, then with successive 5 ml. portions until no further color change is observed in the chloroform layer. The aqueous layer is then

extracted with small portions of chloroform to remove the dithizone. The pH is then adjusted to 8.5 and the usual lead extraction is made.

If the material contains thallium, then lead and thallium in the dithizone extract must be separated or estimated by other means, as for example by spectrographic analysis.

SPECIAL METHODS FOR COMMERCIAL PRODUCTS

DETERMINATION OF LEAD IN AN ORE AS LEAD CHROMATE [19]

Solutions Required. *Potassium Dichromate.*—Make up a hot saturated solution of $K_2Cr_2O_7$. Cool and reserve for use.

Ammonium Acetate.—Measure out 400 ml. of water and 400 ml. of NH_4OH (sp. gr. = 0.9) into a large beaker and add acetic acid (80%) until the solution is neutral; then add sufficient acetic acid (80%) to make the solution 2% acid with acetic (80%).

Acid Ammonium Chloride.—Measure out 300 ml. of water and 300 ml. of NH_4OH (sp. gr. = 0.9) into a large beaker; make just neutral with HCl (sp. gr. = 1.18) and then add sufficient HCl to make the solution 1% acid.

Method.—Weigh from 1 to 2 g. of the dried and finely ground ore into a 250-ml. beaker, add 20 ml. HNO_3 (1 : 1), digest in a warm place for one hour; add 10 ml. H_2SO_4 and evaporate to fumes. Cool, take up with 100 ml. water, boil for 5 or 10 minutes and allow to stand overnight in the cold. Filter and wash with dilute H_2SO_4 (1 : 9). Transfer the precipitate back to the original beaker, set under the funnel and pour through the paper about 60 ml. of boiling ammonium acetate solution.[20] Replace with a clean 300-ml. beaker; boil the solution containing the $PbSO_4$ and filter through the same paper. Wash well with hot water; dilute the filtrate to a volume of 150 ml., add 2 ml. acetic acid (80%), bring to boil, add 20 ml. of the $K_2Cr_2O_7$ solution, again bring to a boil, stir and allow to stand in a warm place for two hours. Filter on a previously prepared and weighed porcelain Gooch crucible, washing two or three times by decantation using boiling water. Finally, transfer all of the precipitate to the Gooch crucible, wash three or four times with boiling water and finally with alcohol. Dry at 105 to 110° C. for one hour; cool and weigh. The increased weight is $PbCrO_4$. Multiply by 0.6375 for lead.[21] (Theoretical factor 0.6411.)

Accuracy.—Duplicate determinations should check within 0.1% of lead.

[19] Standard Method of the National Lead Company.

[20] When appreciable amounts of calcium are present, use 50 ml. of ammonium acetate solution and 50 ml. of acid ammonium chloride solution for the solution of the $PbSO_4$ as described above.

[21] Empirical factor.

DETERMINATION OF LEAD IN BASIC CARBONATE OF LEAD (CORRODED WHITE LEAD)

Basic carbonate, white lead ($2PbCO_3 \cdot Pb(OH)_2$) contains approximately 80% of combined lead and 20% carbonic acid and combined water, with traces of silver, antimony, lead, and other metals. The analysis of basic carbonate, white lead can best be carried out by Walker's method.[22]

Procedure.—" Weigh 1 gram of the sample, moisten with water, dissolve in acetic acid, filter, wash, ignite, and weigh the insoluble impurities. To the filtrate from the insoluble matter add 25 ml. of sulfuric acid (1 : 1), evaporate and heat until the acetic acid is driven off; cool, dilute to 200 ml. with water, add 20 ml. of ethyl alcohol, allow to stand for two hours, filter on a Gooch crucible, wash with 1% sulfuric acid, ignite, and weigh as lead sulfate. Calculate to total lead ($PbSO_4 \times 0.4833 = Pb$) or calculate to basic carbonate of lead (white lead) by multiplying the weight of lead sulfate by 0.8526.

" The filtrate from the lead sulfate may be used to test for other metals, though white lead is only rarely adulterated with soluble substances; test, however, for zinc, which may be present as zinc oxide.

" Instead of determining the total lead as sulfate it may be determined as lead chromate by precipitating the hot acetic acid solution with potassium bichromate, filtering on a Gooch crucible, igniting at a low temperature, and weighing as lead chromate."

LEAD PEROXIDE (PbO_2) AND TRUE RED LEAD (Pb_3O_4) IN COMMERCIAL RED LEAD BY THE THIOSULFATE IODIDE METHOD[23]

(Method of Diehl[24] modified by Topf[25]—not applicable when substances are present, other than oxides of lead, that liberate iodine under conditions given.)[26]

Weigh 1 g. of the finely-ground sample, transfer to a 200-ml. Erlenmeyer flask, add 10 ml. of a mixture of 7 parts by volume of chloroform and 3 parts by volume of c.p. glacial acetic acid; then add as quickly as possible 40 ml. of the " red-lead solution " at room temperature. Rub with the flattened end of a glass rod until nearly all of the red lead has been dissolved; add 30 ml. of water containing 5 or 6 g. of sodium acetate, and titrate at once with 0.1 N sodium thiosulfate, adding the latter rather slowly and keeping the liquid constantly in motion by whirling the flask. When the solution has become light yellow, rub-up any undissolved particles with the rod until free iodine no longer forms, wash off rod, add the sodium-thiosulfate solution until *pale yellow*, add starch solution and titrate until colorless, add decinormal iodine solution until blue color is just restored and subtract the amount used from the volume of sodium thiosulfate that had been added.

[22] P. H. Walker, Bureau of Chemistry Bulletin No. 109, revised, U. S. Dept of Agriculture, pp. 21 and 22.

[23] A.S.T.M. Method.

[24] Dinglers Polytech. J., **246**, 196 (1882).

[25] Z. anal. Chem., **26**, 296 (1887).

[26] **Lead Peroxide.**—If sample contains an appreciable amount of nitrite (nitrate has no effect on method), leach out water-soluble matter, dry residue and determine PbO_2 as above, calculating to basis of original sample.

Calculation.—The iodine value of the sodium-thiosulfate solution multiplied by $0.942 = PbO_2$; the iodine value multiplied by $2.7 = Pb_3O_4$; the PbO_2 value multiplied by $2.866 = Pb_3O_4$.

The "red-lead solution," the sodium-thiosulfate solution and the starch solution shall be prepared as follows:

Red-Lead Solution.—Dissolve in a large beaker (about 1.1 liter) 600 g. of "Tested Purity" crystallized sodium acetate and 48 g. of KI in about 500 ml. of 25% acetic acid solution (made by mixing 150 ml. of glacial acetic acid with 450 ml. of distilled water). Warm the beaker and contents on a steam-bath, stirring occasionally, until a clear solution is obtained. Cool this solution to room temperature, dilute to exactly 1000 ml. with the 25% acetic acid solution and mix thoroughly. If preferred, the red-lead solution may be prepared separately for each titration, as follows: Dissolve 30 g. of the "Tested Purity" crystallized sodium acetate and 2.4 g. of c.p. KI in 25 ml. of the 25% acetic acid solution, warming gently and stirring until a clear solution is obtained. Cool this solution to room temperature, dilute to 40 ml. with the 25% acetic acid solution, and mix thoroughly.

Sodium-Thiosulfate Solution (decinormal).—Dissolve 24.83 g. of c.p. sodium thiosulfate, freshly pulverized and dried between filter paper, and dilute with water to 1 liter at the temperature at which the titrations are to be made. The solution is best made with well-boiled water free from CO_2, or let stand 8 to 14 days before standardizing. Standardize with pure, re-sublimed iodine, as described in Treadwell-Hall, "Analytical Chemistry," Vol. II, p. 602, 1910, and also against pure potassium iodate; the two methods of standardization should agree within 0.1% on iodine value.

Starch Solution.—Stir up 2 to 3 g. of potato starch with 100 ml. of 1% salicylic acid solution, and boil the mixture till starch is practically dissolved, then dilute to 1 liter,[26] or as per Lord.[27]

LEAD PEROXIDE (PbO_2) AND TRUE RED LEAD (Pb_3O_4) IN COMMERCIAL RED LEAD BY HYDROGEN PEROXIDE—PERMANGANATE METHOD[28]

The following is a convenient and relatively accurate method which depends upon the interaction of lead peroxide and of hydrogen peroxide and a titration of the excess of the latter by potassium permanganate.

Treat 1 gram of the sample in a beaker with 15 ml. of nitric acid, specific gravity 1.2 (110 ml. nitric acid, specific gravity 1.42, to 100 ml. of water. This solution should be aerated to free it from all nitrous fumes). Stir the sample until all trace of red color has disappeared. Add from a calibrated pipette or burette exactly 10 ml. of dilute hydrogen peroxide (1 part of 3% hydrogen peroxide to 3.5 parts of water). Add about 50 ml. of hot water and stir until all the lead dioxide has passed into solution. In the case of some coarsely-ground oxides the contents of the beaker may have to be gently heated to effect complete solution. After the oxide has completely passed into solution, dilute with hot water to about 250 ml. volume, and titrate directly with a standard potassium permanganate solution, having an iron value of 0.005. Titrate to the faint pink permanganate color.

[27] "Notes on Metallurgical Analysis," p. 103, 1903.
[28] J. A. Schaeffer, J. Ind. Eng. Chem., 8, 237, 1916.

A blank titration on the hydrogen peroxide solution must now be made. Into a beaker pour 15 ml. of nitric acid having the strength as above given and add exactly the same amount of hydrogen peroxide (10 ml.). Dilute to 250 ml. with hot water and titrate with standard potassium permanganate to a faint pink color.

The difference between the number of ml. of potassium permanganate required for the blank titration and the number required for the red lead titration is the amount of potassium permanganate required for the hydrogen peroxide which was reacted on by the lead dioxide. The difference between the two amounts of potassium permanganate required multiplied by 3.058 gives the percentage of red lead present. To determine the lead dioxide present multiply this difference by 1.067.

The basis of the calculations depends on the fact that each ml. of potassium permanganate solution (iron value, 0.005) is equivalent to 3.058% of true red lead on a one gram sample. A red lead or orange mineral having 100% true red lead content requires 32.7 ml. potassium permanganate solution of the above strength.

It is always advisable to make several blank determinations each day where this analysis is constantly made and when only occasionally used a blank titration should be made before each analysis. The strength of the hydrogen peroxide solution will vary but the permanence of the permanganate solution renders the method accurate over a long period of time.

Standard Potassium Permanganate.—It is necessary to always have a potassium permanganate solution with an iron value of exactly 0.005 if the method described for red lead is used. Dissolve 5.75 grams c.p. salt in two liters distilled water and store in a brown bottle in a dark place for a week or more. By this time all organic matter will have been oxidized and after filtering the solution through an asbestos filter the solution is ready for standardization. As small amounts of MnO_2 destroy the permanence of this solution, it is necessary that it be removed by filtering. The method described in Bureau of Standards Circular No. 40 should be used. This method is as follows:

In a 400-ml. beaker, 0.25 gram of sodium oxalate is dissolved in 200 to 225 ml. of hot water (80–90° C.) and 10 ml. of (1 : 1) sulfuric acid added. The solution is at once titrated with the solution of permanganate, the solution being stirred continuously and vigorously. The permanganate must be added at the rate of 10 to 15 ml. per minute and the last 0.5 to 1 ml. must be added drop by drop, each drop being allowed to decolorize fully before the next is added. The solution should not be below 60° C. by the time the titration is completed. With a permanganate solution having an iron value of 0.005 per ml., 41.66 ml. of the permanganate are required to react with 0.25 gram sodium oxalate.

If the first titration shows that the solution is too strong a small amount of distilled water should be added. To calculate exactly how much water to add divide 41.66 by the number of ml. required in the titration and multiply by the number of ml. remaining in the bottle. The difference between this product and the number of ml. in the bottle will be the volume of water to add.

If the solution is too weak this difference multiplied by 0.00283 will be the grams of potassium permanganate salt to add. After the addition of water or salt the solution should again be titrated and if a titer of 41.66 is not obtained

water or salt added until this titer is obtained. A solution carefully prepared in this manner should keep for months.

NOTE.—Where numerous determinations of true red lead must be made it is convenient to have a burette scaled directly to read in terms of percentage of Pb_3O_4 in the sample. Details for the scaling of the burette in this manner and for using it are given in "Chemical Analysis of Lead and Its Compounds" by Schaeffer, White and Calbeck, 3rd Edition, pages 79 to 81.

RAPID METHOD FOR DETERMINING LEAD IN ZINC ORES OF THE SULFIDE TYPE[29]

The following procedure, a modification of the volumetric molybdate method, is convenient and has proven accurate enough for control work on zinc ores of the sulfide type, such as are found in the Tri-State field, and on "roasted" or oxidized ore.

(a) **Zinc Sulfide Ore.**—Heat a 5 g. sample with 50 ml. dilute nitric acid until the ore is well oxidized. Add 15 ml. concentrated sulfuric acid and keep on hot plate till SO_3 fumes are copiously evolved. Cool and dilute with 300 ml. water. Boil and allow to settle for 4 hours. * Filter through fine filter paper and wash well. Place the paper and contents in the beaker from which the filtration was made and add about 12 ml. of saturated ammonium acetate solution. Heat until all lead sulfate is dissolved and then add 100 ml. water. Titrate with standard ammonium molybdate solution (4.335 g. of the salt dissolved in water and diluted to 1000 ml.), using tannic acid (0.5% solution) as an outside indicator, the end-point being the attainment of a brownish coloration when a drop of the titrated solution is brought into contact with a drop of the indicator.

The size of the sample may be varied to suit its lead content. Thus if the latter is about 0.2%, a 10 g. sample is convenient; for a lead content of 5%, a 2 g. sample is recommended.

Although 1 ml. of molybdate solution made up as above theoretically equals .005 g. lead, the solution should be standardized either against assay litharge or pure lead foil.

(b) **"Roasted," or Oxidized Zinc Ore.**—Digest a 5 gm. sample on hot plate with 40 ml. concentrated sulfuric acid until the ore is completely broken down and until dense fumes of SO_3 are evolved. Cool, add 300 ml. water, heat to complete dissolution of soluble matter, and allow to settle for 4 hours. Then proceed as from point marked * in (*a*) above.

Analysis of Pig Lead.—See Volume II. Alloys.

Lead in Pigments.—Consult the chapter on Paint and Paint Pigments in Volume II.

Tetraethyl Lead.—See Volume II. Petroleum Products.

The contributions of J. R. Sheppard, Consulting Chemist and Metallurgist, Saginaw, Mo., formerly Director of Research, The Eagle-Picher Lead Co., Joplin, Mo., and of W. J. Brown, Chief Analyst of the National Lead Co., to the preliminary revision of this chapter are acknowledged. The final revision was by A. J. Nicklay, Research Chemist, The Eagle-Picher Lead Co. The testing of the accuracy of certain methods was carried out by Lenora White and S. M. Aldredge.

[29] By W. M. Bratton, Hillsboro Zinc Oxide Plant, Eagle-Picher Lead Co.

MAGNESIUM[1]

Mg, *at.wt.* 24.32; *sp.gr.* 1.69–1.75; m.p. 651°; *b.p.* 1110° C.; *oxide* MgO

Magnesium is one of the most abundant of the metals and is widely distributed in nature, occuring only in combined state. The following are the more important ores in which the element occurs: Magnesite, $MgCO_3$; dolomite, $CaCO_3 \cdot MgCO_3$; kieserite, $MgSO_4 \cdot H_2O$; kainite, $MgSO_4 \cdot KCl \cdot 6H_2O$; carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$; in the silicates, enstatite, $MgSiO_3$; talc, $H_2Mg_3(SiO_3)_4$; meerschaum, forsterite, Mg_2SiO_4; titanate, $MgTiO_3$; olivine, $Mg_2SiO_4 \cdot Fe_2SiO_4$; serpentine, $H_4Mg_3Si_2O_9$. It occurs as boracite, $4MgB_4O_7 \cdot 2MgO \cdot MgCl_2$. It is found in sea-water, and in certain mineral waters. It occurs as a phosphate and carbonate in the vegetable and animal kingdoms.

DETECTION

In the usual course of analysis magnesium is found in the filtrate from the precipitated carbonates of barium, calcium, and strontium. The general procedure for removal of the preceding groups may be found in the section on Separations given on the following page, 531. Magnesium is precipitated as white magnesium ammonium phosphate, $MgNH_4PO_4$, by an alkali phosphate, Na_2HPO_4, $NaNH_4HPO_4$, etc., in presence of ammonium chloride and free ammonia. The precipitate forms slowly in dilute solution. This is hastened by agitation and by rubbing the sides of the beaker during the stirring with a glass rod. Crystals soon appear on the sides of the beaker in the path of contact, and finally in the solution.

Procedure.—To the filtrate from calcium precipitation by ammonium oxalate add 5 ml. of 15 N NH_4OH and 25 ml. of Na_2HPO_4 solution and stir.

[1] The Romans were familiar with the oxide of magnesium, "magnesia alba." The sulfate was obtained by Grew from a natural spring in Epsum, England. The metal was obtained in impure form by Davy in 1808. The metal in powdered form is used in photographic flash lights, in flares, the ribbon is likewise used. The element is used in alloys, magnalium is an alloy of aluminum and magnesium; duraluminum, an alloy of aluminum, copper, silicon with a small percentage of magnesium. The alloys are employed where lightness and strength are required, for example in aircraft. The oxide magnesia is a refractory material and an insulator, magnesium oxychloride is used in stucco and as an insulator. Magnesium carbonate is the basis of silver polishes and certain toothpowders. The hydroxide, milk of magnesia, is a mild remedy for acidity of the stomach. Asbestos is a silicate of magnesium, likewise talc and soapstone. The carbonate and sulfate are valuable pharmaceutical products.

If no precipitate forms, let the mixture stand for at least half an hour, stirring frequently. A white crystalline precipitate indicates the presence of magnesium. Filter and wash the precipitate with alcohol. *Confirm* as follows:—Treat the precipitate or a small portion, if the amount is large, with 5 ml. of 2 N H_2SO_4, and to the solution add 10 ml. of alcohol and stir vigorously. If a precipitate forms ($BaSO_4$ etc.) filter off, saving the filtrate. To the filtrate (or solution, if no precipitate forms) add 10 ml. of water, 20 ml. of NH_4OH and 5 ml. of Na_2HPO_4 (10% soln.) and let the mixture stand at least half an hour. A white crystalline precipitate confirms the presence of magnesium.

Baryta or lime water added to a solution containing magnesium produces a white precipitate of magnesium hydroxide.

Both the phosphate and the hydroxide of magnesium are soluble in acids.

Delicate Colorimetric Test for Magnesium.—Titan yellow G [2] has been proposed by Kolthoff [3] as a reagent for the detection of magnesium. To 10 ml. of the solution to be tested 0.1 to 0.2 ml. of a 0.1% solution of the indicator in water and about 0.25 to 1 ml. 4 N sodium hydroxide are added. In the absence of magnesium the mixture has a brownish-yellow color; if 5 mg. magnesium per liter are present, the solution turns nicely red, with 1 mg. Mg p. l. orange. If a blank without Mg is used for comparison, 0.2 of a mg. Mg p. l. can be detected (sensitivity). Small amounts of calcium intensify the color of the magnesium reaction product, which must be considered in the application of the reagent to the colorimetric determination of magnesium in presence of calcium salts. The reaction is very suitable for the detection and approximate estimation of traces of magnesium in alkali salts. Similarly it can be used for the detection of this element in calcium salts. In testing calcium carbonate for the presence of magnesium, the most delicate procedure is to dissolve this salt in a small excess of hydrochloric acid then add the indicator and make alkaline with 1 to 2 ml. 4 N sodium hydroxide, a precipitate of calcium carbonate not interfering. Fifty mg. of calcium carbonate are treated with 4 drops 4 N HCl, 10 ml. of water and 0.2 ml. 0.1% titan yellow, and 1 to 2 ml. 4 N sodium hydroxide are added. In the presence of 0.1% magnesium in the calcium carbonate a bright red color appears and even 0.01% of magnesium can be detected by comparing with a blank. In the so called "chemically pure" commercial products of calcium carbonate, the presence of magnesium is easily shown.

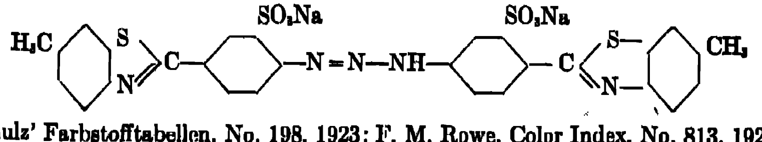
Nickel and cobalt must be absent as they give the same reaction as magnesium. Consult original article.

DETECTION WITH p-NITROBENZENE-AZO-RESORCINOL [4]

Reagent.—0.1 g. of the compound in 100 ml. of 1% NaOH. The reagent is stable for a few months.

Test.—All other metallic ions than magnesium and the alkalies should be removed; ammonium salts must be removed before the test is made. The

[2] I. Titan yellow G: Sodium salt of the diazoamino compound of dehydro-thio-p-toluidinsulfonic acid (or the mixed diazoamino compound of dehydro-thio-p-toluidinsulfonic acid and primuline dehydro-thio-p-toluidinsulfonic acid).



(Schulz' Farbstofftabellen, No. 198, 1923; F. M. Rowe, Color Index, No. 813, 1924.)

[3] I. M. Kolthoff, Biochem. Z., 185, 344, 1927.

[4] Suitsu and Okuma, J. Soc. Chem. Ind. Japan, 29, 132 (1926); Ruigh, J. Am. Chem. Soc., 51, 1456 (1929); Engel, ibid., 52, 1812 (1930).

solution (10 ml.) that may contain magnesium is treated with 1 drop of the reagent and then made strongly alkaline with NaOH. The presence of magnesium is indicated by a blue color or precipitate.

ESTIMATION

The element is determined in the complete analysis of a large number of substances; in the analysis of ores, minerals, rocks, soils, cements, water, etc.

In analytical procedures magnesium passes into the filtrate with the alkalies after separating the elements of the HCl, H_2S, $(NH_4)_2S$ and $(NH_4)_2CO_3$ groups, where it is separated from the alkalies by precipitation as magnesium ammonium phosphate. Should arsenates or phosphates be present in excess of the amounts taken care of by the iron and aluminum (etc.) present, magnesium will come down with the ammonium precipitate and will be weighed as iron and aluminum oxides, unless provision is made to avoid this.

Decomposition of the substances containing magnesium and separation of the element are given later.

PREPARATION AND SOLUTION OF THE SAMPLE

In solution of the material it will be recalled that the metal is soluble in acids and is also attacked by the acid alkali carbonates. It is soluble in ammonium salts. The oxide, hydroxide, and the salts of magnesium are soluble in acids. Combined in silicates, however, the substance requires fusion with alkali carbonates to bring it into solution.

General Procedure for Ores.—One gram of the ore is treated with 20 ml. of conc. hydrochloric acid and heated gently until the material is decomposed. If sulfides are present, 5 to 10 ml. of conc. nitric acid are added and the material decomposed by the mixed acids. If silicates are present and the decomposition is not complete by the acid treatment, the insoluble material is decomposed by fusion with sodium carbonate, or the entire sample may be fused with the alkali carbonate, the fusion is dissolved in hydrochloric acid and taken to dryness. Silica is dehydrated as usual by heating the residue from the evaporated solution. This is taken up with 50 ml. of water containing about 5 ml. conc. hydrochloric acid, the silica filtered off and, after removal of the interfering substances according to procedures given under the next section on Separations, magnesium is determined as directed in the sections on Methods.

SEPARATIONS

Removal of Members of the Hydrogen Sulfide Group. Copper, Lead, Bismuth, Cadmium, Arsenic, etc.—The filtrate from silica [5] is diluted to about 200 ml. and hydrogen sulfide gas passed in until the members of this group are completely precipitated. The sulfides are filtered off and washed with H_2S water and the filtrate and washings concentrated by boiling. This treatment is seldom necessary in analysis of many silicates and carbonates in which these elements are absent.

Removal of Iron, Aluminum, Manganese, Zinc, etc.—The concentrated filtrate from the hydrogen sulfide group, or in case the treatment with hydrogen sulfide was not required, the filtrate from silica, is boiled with a few ml. of nitric acid to oxidize the iron (solution turns yellow), about 5 ml. of concentrated hydrochloric acid added, and the solution made alkaline to methyl orange by adding NH_4OH, drop by drop until a yellow color is obtained. If zinc, cobalt, and nickel are present, these are best removed as sulfides by passing hydrogen sulfide into the ammoniacal solution.

Separation of Magnesium from the Alkaline Earths.—The alkaline earths are precipitated either as oxalates, recommended when considerable calcium is present, or as sulfates, recommended in presence of a large proportion of barium, the magnesium salts being soluble. A double precipitation is necessary to recover magnesium occluded by calcium oxalate. Magnesium is precipitated from the filtrates as a phosphate, according to directions given later. Details of the separation of magnesium from the alkaline earths may be found in the chapter on Barium.

An excellent procedure for the separation by means of sulfuric acid is to evaporate the solution to dryness, concentrating first in a porcelain dish and finally to dryness in a platinum dish, and then adding about 50 ml. of 80% alcohol and sufficient sulfuric acid to combine with the alkaline earths and magnesium, with slight excess. This precipitates barium, strontium, and calcium as sulfates, while the greater part of the magnesium is in solution. After settling, the precipitate is filtered and washed free of sulfuric acid by means of absolute alcohol, then with 40% alcohol to remove any magnesium sulfate remaining with the precipitate. Magnesium is determined in the filtrate by expelling the alcohol by evaporation, and then precipitating as magnesium ammonium phosphate according to directions given for the determination of this element.

Separation of Magnesium from the Alkalies.—Members of the HCl, H_2S, $(NH_4)_2S$ and $(NH_4)_2CO_3$ groups being removed, magnesium is quantitatively precipitated as phosphate free from the alkalies by addition of a soluble phosphate (Na_2HPO_4, $NaNH_4HPO_4$, $(NH_4)_2HPO_4$ etc.) to the ammoniacal solution. Details are given under the gravimetric method that follows later.

Separation of Magnesium by Precipitation with 8 Hydroxyquinoline.[6]—The reagent precipitates the following elements in acid-acetate solution: Cu, Bi, Cd, Al, Zn, quantitatively, and Ag, Hg, Pb, Sb, Va, U, Fe, Ta, Ti, Co, Ni, Cb, Mn

[5] See previous paragraph.

[6] Z. H. Skraup, Monatsh. chem., 2, 139, 518, 1881; *ibid.*, 3, 381, 531, 1882. R. Berg, J. prakt. Chem., 115, 178, 1927; J. Robitschek, J. Am. Ceram. Soc., 11, 587, 1928; I. M. Kolthoff and E. B. Sandell, J. Am. Chem. Soc., 50, 1900, 1928; G. E. F. Lundell and H. B. Knowles, Bur. Standards J. Research, 1929.

and Zr from acetic acid solution, with exception of Ag, all of above and in addition Ba, Be, Ca, Mg and Sn in ammoniacal solution, effecting separation from the alkalies. After the removal of the interfering elements (see list above) by precipitation with HCl, H_2S, $(NH_4)_2S$ and removal of the alkaline earths, magnesium is precipitated by the reagent as follows:—The solution containing 0.1 g. MgO equivalent per 100 ml. and sufficient NH_4Cl to prevent precipitation of $Mg(OH)_2$, is heated to about 70° C. and 8 hydroxyquinoline reagent (5 g. powder per 100 ml. 2 N acetic acid) is added to complete precipitation of magnesium and 10% excess to the feebly acid solution and then sufficient NH_4OH to make the solution alkaline. (The excess of the reagent colors the solution yellow.) The solution is settled, filtered, washed with dilute NH_4OH (1 : 40), dried at 130–140° C. and weighed as $Mg(C_9H_6ON)_2$, containing 12.91% of MgO.

Separation of Magnesium from Iron and Aluminum.—Magnesium phosphate is precipitated in presence of tartaric acid.

GRAVIMETRIC DETERMINATION OF MAGNESIUM

PRECIPITATION OF MAGNESIUM AS MAGNESIUM AMMONIUM PHOSPHATE AND ESTIMATION AS PYROPHOSPHATE [7]

Magnesium is determined in the filtrate from the alkaline earths after the removal of members of the HCl, H_2S, $(NH_4)_2S$ and the alkaline earths, which would interfere with its determination. Should phosphates be present in the original material, magnesium is apt to precipitate with iron and aluminum when the solution is made alkaline with NH_4OH. The phosphate radical may be removed by precipitation from an acid (HNO_3) solution by ammonium molybdate. The phosphate is filtered off and washed with water containing HNO_3 (2%). The free acid is neutralized by adding NH_4OH in presence of methyl orange indicator until a yellow color develops. The solution should contain sufficient NH_4Cl to prevent precipitation of $Mg(OH)_2$ by NH_4OH. If manganese is present it must be removed by precipitation with H_2S or by Br in ammoniacal solution. Calcium is removed by a double precipitation as oxalate. If barium is present it is removed as $BaSO_4$ by precipitation with H_2SO_4. Should molybdenum be present it may be removed as sulfide. The solution should contain sufficient NH_4Cl to prevent precipitation of $Mg(OH)_2$, but a large quantity is undesirable. Since the separations may lead to loss of mag-

[7] L. L. de Koninck, Z. anal. Chem., 29, 165, 1890. Alice W. Epperson, J. Am. Chem. Soc., 50, 324, 1928. J. M. McCandless and J. I. Burton, J. Ind. Eng. Chem., 19, 496, 1927.

nesium through occlusion and adsorption, double precipitations should be made. Finally, the precipitation should be made under conditions that would give $MgNH_4PO_4 \cdot 6H_2O$ uncontaminated by $Mg_3(PO_4)_2$, $Mg(NH_4)_4(PO_4)_2$, or $Mg(OH)_2$. The first and last would lead to low results, the second to high results, and a mixture to an uncertain error. A double precipitation is recommended, the precipitations being made by adding the soluble phosphate reagent to a slightly acid solution and then making alkaline with NH_4OH. Diammonium phosphate is a satisfactory precipitant. It is interesting to note that a high concentration of $(NH_4)H_2PO_4$ and NH_4Cl results in a precipitate (phosphate of ammonia) forming which may be mistaken for magnesium. This dissolves on dilution. The magnesium salt is ignited to $Mg_2P_2O_7$.

Reactions.—$(NH_4)_2HPO_4+MgCl_2+NH_4OH=MgNH_4PO_4+2NH_4Cl+H_2O$ and $2MgNH_4PO_4$ ignited$=2NH_3+H_2O+Mg_2P_2O_7$.

Procedure.—The combined filtrates from the double precipitation of calcium, free from interfering elements, are neutralized with HCl and made faintly acid. The solution is diluted so as to contain not over 0.1 g. MgO per 100 ml. and for each 100 ml. 20 ml. of a 10% solution of $(NH_4)HPO_4$ solution are added. The solution is stirred vigorously (avoiding touching the sides of the vessel with the stirring rod) and while stirring NH_4OH is added dropwise (conveniently from a burette) until the free acid is neutralized and a further addition of 10 ml. per each 100 ml. of solution present. The precipitate is allowed to settle at least four hours, preferably overnight, and is filtered through filter paper and washed with cold dilute (1 : 20) solution of NH_4OH.

The precipitate is dissolved in warm dilute HCl (1 : 4), catching the solution in the beaker, in which the precipitation was made, dissolving any magnesium precipitate adhering to the beaker and stirring rod. The solution is diluted to 100–150 ml., 1–2 ml. of the diammonium phosphate reagent added followed by NH_4OH added drop by drop as before until the solution is alkaline and now 5 ml. in excess of each 100 ml. of solution. The precipitate is allowed to settle and stand for four hours or more and is filtered onto a paper filter (ashless) and washed with NH_4OH (1 : 20), carefully cleaning out the beaker of all adhering precipitate, adding this to the filter. (Some of the phosphate is apt to adhere to the walls of the beaker, hence the precaution.)

The filter is folded and with its contents placed in a crucible that has been previously weighed. After drying in an oven the paper charred by gentle heating over a low flame. The heat is gradually increased and finally to the full blast of a flame at a temperature of 1000° C. until a constant weight is obtained. The residue is $Mg_2P_2O_7$.

Factors. $Mg_2P_2O_7 \times 0.3621 = MgO$ or $0.2184 = Mg$ or $\times 0.7574$
$= MgCO_3$ or $\times 1.0812 = MgSO_4$ or $\times 2.2139 = MgSO_4 \cdot 7H_2O$.

Notes on Magnesium.—The ignition is conducted gently at first to gradually oxidize the carbon that the precipitate contains. With rapid ignition the particles are inclosed in the mass in a form that it is almost impossible to completely oxidize, so that the final residue is gray instead of white. L. L. de Koninck [8] considers that the blackening of the precipitate is frequently due to the presence of organic bases in commercial ammonia and its salts, rather than to the fibers of filter paper occluded in the mass. With caution, the filter and residue may be ignited wet, the heat being low until the filter completely chars and then being increased, with the cover removed, until the residue is white.

[8] Z. anal. Chem., 29, 165 (1890).

Impurities.—The precipitate may contain traces of lime that remained soluble in ammonium oxalate. This may be determined by dissolving the pyrophosphate in dilute sulfuric acid followed by addition of 9 to 10 volumes of absolute alcohol. Calcium sulfate, $CaSO_4$, precipitates and settles out on standing several hours. It may be filtered off, dissolved in hydrochloric acid and precipitated as oxalate in the usual way and so determined.

A residue remaining after treating the pyrophosphate with acid is generally SiO_2.

The presence of manganese may be detected by dissolving the magnesium pyrophosphate, $Mg_2P_2O_7$, in nitric acid and oxidizing with sodium bismuthate. (See method under Manganese.)

Properties of Ammonium Magnesium Phosphate.—Readily soluble in dilute acids. One hundred ml. of pure water at 10° C. will dissolve 0.0065 gram. The presence of ammonia greatly decreases the solubility of the salt, e.g., 2.5% ammonia decreases the solubility to 0.00006 gram MgO per 100 ml. The presence of ammonium salts increase the solubility of the precipitate, e.g., 1 gram of ammonium chloride will increase the solubility to 0.0013 gram MgO.[9]

A large amount of NH_4Cl tends to prevent precipitation of magnesium so that its removal may be advisable. This may be accomplished by J. Lawrence Smith method [10] by making the solution slightly acid with HCl and adding 2–3 ml. concentrated HNO_3 per gram NH_4Cl present, covering the beaker until the evolution of gas has ceased and then evaporating to dryness.[11]

A pink color of the precipitate indicates contamination by Mn.

Hillebrand and Lundell [12] claim that asbestos should not be used as a filtering medium for the magnesium precipitate as some types are attacked by alkaline solvents containing soluble phosphates.

VOLUMETRIC DETERMINATION OF MAGNESIUM

TITRATION OF THE AMMONIUM MAGNESIUM PHOSPHATE WITH STANDARD ACID

The procedure known as Handy's volumetric method for magnesium,[13] depends upon the reaction $MgNH_4PO_4 + H_2SO_4 = MgSO_4 + NH_4H_2PO_4$. An excess of standard sulfuric acid is added to the precipitate and the excess of acid titrated back with standard sodium hydroxide.

Procedure.—The method of precipitation of the magnesium ammonium phosphate is the same as has been described under the gravimetric method.

[9] Am. J. Sci. (3), 5, 114, 1873.

[10] Am. J. Sci., 15, 94, 1853.

[11] J. L. Smith, Am. Chemist, 111, 201, 1873. A. C. Langmuir, J. Am. Chem. Soc., 22, 104, 1900.

[12] "Applied Inorganic Analysis," John Wiley & Sons, New York.

[13] James Otis Handy, J. Am. Chem. Soc., 22, 31 (1900).

The precipitate is washed several times by decantation with 10% ammonium hydroxide solution (1 part NH_4OH, sp. gr. 0.90 to 9 parts water), and finally on the filter. After draining, the filter is opened out, the moisture removed as much as possible by means of dry filter papers. The residue may be dried in the room for about forty-five minutes or in the air oven at 50 to 60° C. for fifteen to twenty minutes.[14] When the filter has dried, ammonia will have been expelled. The substance is placed in a dry beaker, N/10 sulfuric acid added in excess (methyl orange indicator), the solution diluted to 100 ml. and the excess of acid titrated with N/10 sodium hydroxide.

$$\text{One ml. N/10 } H_2SO_4 = 0.002016 \text{ gram MgO.}$$

OXINE METHOD FOR DETERMINATION OF MAGNESIUM

The details of the precipitation of aluminum by Berg's method with 8-oxyquinoline has been described; in acids magnesium remains in solution. On making the solution alkaline magnesium precipitates with the addition of this reagent. Interfering elements must be absent, the alkalies may be present in the solution. The filtrate from the oxalate precipitation is taken for the determination of magnesium.

Procedure.—Fifty to one hundred ml. of solution containing the magnesium, free from interfering elements, and containing 1–2 ml. of 2 N NH_4Cl and about 1 ml. of free 6 N NH_4OH are heated to boiling and the oxine solution added, drop by drop, the precipitate allowed to settle, then filtered off, washed and weighed as $Mg(C_9H_6NO)_2$.

In an 0.001 M. solution magnesium can be determined by this method, accurately to 1% according to Kolthoff.

THE SAMPLING AND ANALYSIS OF CRUDE, CAUSTIC AND *DEAD-BURNED MAGNESITE*[15]

By H. E. CLEAVES

Sampling.—In pulverizing *dead-burned* magnesite it should be kept in mind that this material is very abrasive and that any grinding between iron surfaces, such as in a disc pulverizer or on a bucking board, will result in contamination of the sample with a considerable quantity of iron.

The method of sampling used in this laboratory is as follows: The sample from the bin is cut to about 15 lbs. through a Jones Sampler. This sample is crushed through a small jaw crusher and cut through a Jones sampler to about 1000 grams. This is crushed to pass an 8 mesh screen, using a Spiegel mortar made of case-hardened tool steel (Arthur H. Thomas, Cat. No. 7320). The material is crushed in the mortar by hammering the pestle, avoiding any grinding action. The sample is then cut to about 100 grams through the Jones sampler, crushed to pass a 100 mesh screen, using the Spiegel mortar, and finally cut to about 25 grams by quartering on an oil cloth.

[14] Low, "Technical Methods of Ore Analysis," John Wiley & Sons, New York.
[15] Method of the North West Magnesite Company.

Analysis. *Ignition Loss.*—Weigh 1 gram into a platinum crucible, weigh crucible and sample, heat in electric muffle at 1000° C. for 30 minutes, cool and weigh. Loss in weight $\times 100$ gives ignition loss in per cent.

Silica.—Weigh 0.5 gram into a platinum crucible containing about 2 grams of anhydrous sodium carbonate, mix, cover and fuse over a gas flame or in an electric muffle. Cool, loosen by squeezing the sides of the crucible, transfer to a 3 inch evaporating dish, cover with a watch glass and add sufficient hot dilute HCl to dissolve the fusion. Dissolve the material remaining on the cover and in the crucible with a little hot dilute HCl, pour into the evaporating dish and rinse crucible and cover with warm water, using finger to loosen any silica which may cling to the crucible. When fusion is dissolved remove and wash watch glass and evaporate solution to dryness over a water bath. If, when about half evaporated, any material remains undissolved on the bottom of the dish, stir it up with a stream of hot dilute HCl from a wash bottle. When dry bake in an oven at 110–118° C. until no odor of HCl can be detected. Do not heat above 118° C.; the silica may combine with the magnesia above this temperature, causing low results. When sufficiently baked dissolve with a small quantity of hot dilute HCl, dilute with twice the quantity of hot water, heat to boiling and filter through an 11 cm. No. 40 Whatman paper into a 250 ml. beaker, loosening silica clinging to the dish with a policeman and rinsing dish into filter with hot water. Wash filter 8 times with hot water, circling wash stream around top of paper. Burn filter in a weighed platinum crucible, cool, and weigh. Moisten silica in crucible with a drop of water, add a drop of dilute H_2SO_4, add about 1 ml. of HF, evaporate on hot plate until free from SO_3 fumes, ignite in muffle at 1000° C., and weigh. Loss in weight multiplied by 200 gives per cent of silica. Weight of residue in crucible, obtained by subtracting weight of empty crucible from weight of crucible after volatilization of silica, is added to weight of R_2O_3.

Iron and Alumina (R_2O_3).—To filtrate from the silica add about 4 grams of NH_4Cl and a few drops of rosolic acid solution, heat to boiling, add a little paper pulp, make very slightly ammoniacal with dilute ammonia, as shown by faint pink color of rosolic acid, and filter through an 11 cm. No. 31 Whatman paper into a 600 ml. beaker. Without washing, transfer paper with precipitate back into same 250 ml. beaker, add about 25 ml. of hot dilute HCl, pulp paper by stirring with a glass rod, add about 100 ml. of hot water and a few drops of rosolic acid solution, and reprecipitate by making faintly ammoniacal with dilute ammonia. Filter through an 11 cm. No. 31 Whatman paper into previous filtrate, wash beaker and paper 4 times with 1% NH_4NO_3 solution. Transfer filter and precipitate to a No. 2 annealing cup and ignite in a muffle, cool, empty onto balance pan and weigh. Add weight of residue from silica determination to this weight, subtract weight of 2–11 cm. No. 31 Whatman papers and multiply by 200 to get % of R_2O_3.

Lime.—Make filtrate from above slightly acid, add about 8 grams of NH_4Cl, and 75 ml. of ammonium oxalate solution, stir to dissolve NH_4Cl, dilute to within 1/2 in. of top of beaker, make slightly ammoniacal and let stand over night. Filter through an 11 cm. No. 30 Whatman paper, wash beaker and paper once with water, dissolve precipitate by filling funnel twice with hot, dilute HCl, letting solution run back into same 600 ml. beaker, wash paper at least 6 times or until volume of solution in beaker is about 300 ml.,

using hot water. Add ammonia until solution is faintly acid, heat to boiling, add about 25 ml. of ammonium oxalate solution, make faintly ammoniacal, remove to asbestos board on hot plate where solution will keep hot but will not boil. When precipitate has settled, remove from hot plate and when cool filter through an 11 cm. No. 30 Whatman paper. Wash beaker 3 times and paper 12 times more with water, circling wash stream around top of paper. To beaker add about 50 ml. of cold water, 25 ml. of dilute H_2SO_4, dilute to about 300 ml. with boiling water, drop paper containing calcium oxalate precipitate into beaker and stir, without pulping paper. Titrate to a faint pink with standard potassium permanganate solution. Ml. of permanganate $\times$ lime factor $\times 200$ gives % of lime.

Magnesia.—Ordinarily the difference between the sum of the above determinations and 100 is reported as magnesia. Where a direct determination of the magnesia is required the following is the method used: Make the combined filtrates from both lime precipitations up to 1000 ml. in a volumetric flask, and take a 200 ml. aliquot. Heat to 50° C., add from a pipette drop by drop, with stirring, 10 ml. of cold saturated ammonium phosphate solution. If a precipitate does not form with the first few drops add a little ammonia. In a few minutes stir and add about 10 ml. of paper pulp. Then, with stirring, add 25 ml. 1 : 1 NH_4OH. Let stand over night, filter through an 11 cm. No. 40 Whatman paper. Dissolve precipitate with hot dilute HCl, letting solution run back into same beaker, wash with hot water until volume is about 150 ml., add a few drops of rosolic acid indicator, add 1 ml. ammonium phosphate solution, then make alkaline with dilute ammonia, stirring until precipitate forms. In a few minutes stir and add 10 ml. paper pulp. Then with stirring add 20 ml. 1 : 1 ammonia. Let stand over night. Filter through an 11 cm. No. 40 Whatman paper. Wash with 2 funnels of cold 1 : 10 ammonia, drain well, place filter in a No. 2 annealing cup, place in front of muffle till charred and paper is burned, finish to 1000° C. Grams $Mg_2P_2O_7 \times .3621 \times 1000$ gives % MgO.

Solutions. ***Dilute HCl.***—One part conc. HCl to 3 parts water.

Dilute NH_4OH.—One part conc. NH_4OH to 3 parts water.

Dilute H_2SO_4.—One part conc. H_2SO_4 to 3 parts water.

Rosolic Acid Solution.—One gram rosolic acid in 100 ml. 75% grain alcohol.

Ammonium Nitrate Wash Solution.—Ten grams ammonium nitrate to a liter of water.

Ammonium Oxalate Solution.—Sixty grams ammonium oxalate to a liter of water. Keep solution warm with heat from a 100 watt electric light to prevent crystallization.

Potassium Permanganate Solution.—Solution used in this laboratory is approximately 1/28 normal so that 1 ml. equals 0.001 grams CaO or 0.2% on a 0.5 gram sample. Made by dissolving 11 gm. $KMnO_4$ to each liter of water, standardizing with Bureau of Standards sodium oxalate, diluting to give required factor and restandardizing.

Paper Pulp.—Make by moistening quantitative filter paper clippings with water, add conc. HCl and stir vigorously. Add water, filter through Büchner funnel, wash with hot water to free from acid. Put pulp in container, add water, shake to disintegrate. Add water till consistency is right to pour easily.

When lime is precipitated as oxalate, in the presence of considerable quantities of magnesia, the precipitate will be contaminated with magnesium oxalate, the amount of contamination increasing with increased concentration of undissociated magnesium oxalate. The ammonium oxalate added, if ionized will tend to prevent ionization of the magnesium oxalate, as the two salts contain a common ion. A considerable quantity of ammonium chloride is added, therefore, to decrease the ionization of the ammonium oxalate, thus decreasing the oxalate ions in the solution and increasing, as a result, the dissociation of the magnesium oxalate.

As dilution also increases the dissociation of the magnesium oxalate, as large a volume as possible within reason should be used when precipitating the lime. A volume of 550 ml. is used in the laboratory for the first precipitation and about 400 ml. for the second.

ANALYSIS OF MAGNESIA[16]

1. **Loss on Ignition.**—A 2.0000 gram sample is ignited to constant weight with a Fisher burner.

2. **Decomposition.**—1.0000 gram mixed with approximately an equal weight of reagent Na_2CO_3 in a platinum crucible is sintered with a Bunsen burner. The cake is dissolved in an excess of dilute $HClO_4$ sufficient to provide an excess for refluxing to dehydrate the silica.

3. **Silica.**—Double dehydration with $HClO_4$ with intervening filtration. The silica is corrected for impurities with HF and H_2SO_4.

4. **R_2O_3.**—Double precipitation with NH_4OH.

5. **Other Constituents.**—Fe_2O_3, TiO_2, P_2O_5, etc., determined as in standard methods for rock and clay analysis. The iron is reduced to Fe^{++} and titrated with $K_2Cr_2O_7$ using sodium diphenylamine sulfonate as an indicator.

6. **CaO.**—Calcium is separated by triple oxalate precipitation.

7. **MgO.**—Ammonium salts in the combined filtrates from CaO destroyed with HNO_3. Solution made up to definite volume and aliquots equivalent to .2000 or .2500 gram MgO twice precipitated as phosphate, taking precautions suggested by Lundell and Hoffman.[17] The $Mg_2P_2O_7$ is corrected for CaO and MnO content.

More frequently MgO is not determined directly.

PROCEDURE FOR THE DETERMINATION OF CALCIUM IN BURNED MAGNESITE[18]

To a 1.000 g. sample in a 250 ml. Pyrex beaker add 5 ml. of water and 10 ml. of 60% perchloric acid, then heat on a steam bath until the solvent action is complete. Fume off the excess of $HClO_4$ by placing the beaker on a high temperature hot plate, the last traces of $HClO_4$ being removed by heating the wall of the beaker with a burner flame. No damage is done if some of the

[16] Outline of procedure used by the Norton Co., Worcester, Mass. Courtesy of M. O. Lamar.

[17] Bur. Stand. Jour. Res., 5, 279, 1930.

[18] Caley and Elving, Ind. Eng. Chem., Anal. Ed. 10, 264 (1938).

magnesium perchlorate is dehydrated or decomposed by this treatment. After cooling, dissolve the salts in about 20 ml. of water, filter off the silica and wash successively with small portions of hot water. To save time in evaporation the volume of the wash water should not exceed 50 ml. The filtrate and washings are received in a 250 ml. beaker. Evaporate the solution to 9 ml., and add 1 ml. of dilute (1 : 4) sulfuric acid, cool and then add very slowly from a pipette 90 ml. of pure methanol (CH_3OH). Allow the vessel to stand at least one hour, then filter off the precipitated calcium sulfate on a weighed porcelain filter crucible. Wash with successive small portions of 90% CH_3OH. About 50 ml. will be required. A rubber policeman is used to transfer the last traces of the precipitate to the filter crucible. Wipe off the outside of the crucible with a cloth moistened with benzene to remove any rubber dissolved by the action of the CH_3OH on the rubber crucible holder. Dry the crucible at 110° C. for 30 minutes, then place it in a muffle or crucible furnace and heat for 30 minutes at 400–500° C. Cool and weigh. The weight of $CaSO_4$ in grams $\times$ 41.19 gives the percentage of CaO in the sample.

The amount of sodium and potassium present should not exceed a few milligrams since they form slightly soluble double sulfates with calcium. The above procedure is valid when the R_2O_3 content of the material does not exceed 3 to 4%. With higher percentages of these oxides much longer periods of time may be necessary between precipitation and filtration.

The procedure for the determination of calcium in a limestone or dolomite is nearly the same as that for the determination of calcium in a burned magnesite. For all materials that contain more than 5% of calcium the following slight modification is advisable:

Remove the silica as described for calcined magnesia. To the filtrate and washings after the removal of the silica, add 1 or 2 ml. of the dilute sulfuric acid. Evaporate the solution to 5 ml., add 15 ml. of water and then add very slowly 180 ml. of pure CH_3OH while stirring constantly. Filter after 1 hour.

METHODS FOR THE ANALYSIS OF MAGNESIUM ALLOYS[19]

ALUMINUM

Aluminum is one of the most important constituents of the present magnesium alloys, the amounts varying up to 12%, and in special cases even higher. The alloys are quite soluble in acids, usually being dissolved in either hydrochloric or sulfuric acid, depending upon the method of analysis.

[19] Abridged by the Editor (N. H. F.) from Methods of the Dow Chemical Co., Midland, Mich., supplied by the courtesy of A. W. Beegetoor, Chief Analytical Chemist.

The standard method of analysis is the gravimetric, based upon the precipitation of $Al(OH)_3$ with ammonia and burning to Al_2O_3. This method is slow and subject to considerable error unless handled by an expert, and there may prove to be appreciable variation among different analysists. It is best to make up known standards and check back against them frequently.

A successful potentiometric titration of aluminum in magnesium alloys may be made with the aid of a vacuum tube potentiometric machine and an antimony electrode, eliminating the necessity to plot the readings.

Potentiometric Determination

Solutions.—(1) Brom phenol blue indicator, .04%. Weigh out .40 gm. into a mortar, add 8.25 ml. of N/10 NaOH and mix until solution is complete. Transfer to a one-liter volumetric flask and make to volume with distilled water.

(2) N/1 NaOH.

Procedure.—Weigh accurately a sample of the proper size (4%—2.8–3.3 gm. 6%—1.9–2.3 gm. 8%—1.5–1.7 gm. 10%—1.3–1.5 gm. 12%—1.1–1.3 gm.) into a 250-ml. beaker. Cover the sample with 25 ml. of water and add conc. HCl. (For 4% and 6% alloys, use 8 ml. HCl per gm. of sample, adding it in small portions and allowing sufficient time for it to react between each addition. For 8% and higher, add 8 ml. per gm. of sample and ½ ml. in excess; the ½ ml. excess may be eliminated for any alloy if, in the experience of the analyst, it is found to be unnecessary to give a 10-ml. back-titration of excess acid.) After the sample has dissolved cool and dilute to 100 ml., add 2 ml. of brom phenol blue indicator and NH_4Cl (for 4% add 10 gm.; for 6% add 7 gm.; and all other 5 gm.). Titrate with N/1 NaOH to the blue endpoint, using the stirrer of the potentiometer machine to stir the solution. Stop the stirrer and heat to boiling. Start the stirrer and continue to heat so that the temperature remains *just below* the boiling point. Titrate with N/1 NaOH to the potentiometric endpoint and calculate the per cent aluminum present by the following formula:

$$\frac{\text{ml. N/1 NaOH} \times .00899 \times 100}{\text{sample weight} \times .819} = \%\ \text{Al}$$

(The empirical factor 0.819 applies up to alloys containing 12% Al.)

Gravimetric Determination

Solutions.—(1) Dilute NH_4OH. One part of conc. NH_4OH to 4 parts of water.

(2) Methyl red indicator. The indicator is made by boiling a small amount of methyl red powder with water and decanting to a small bottle. About 5 ml. of this solution should be used.

(3) Dilute HCl. One part conc. HCl to 4 parts of water.

(4) 2% NH_4Cl solution. 20 gm. per 980 ml. H_2O.

Procedure.—Weigh accurately a 5-gm. sample into a 400-ml. beaker. Add 20 ml. of conc. H_2SO_4 and with the cover glass in place dissolve by slowly adding water from a wash bottle. Do not allow the reaction to proceed too rapidly. If there is much residue when the sample is dissolved, filter immediately through

a rapid qualitative paper into a 250-ml. volumetric flask.[20] If there is only a slight residue, add nitric acid to clear and make to volume without filtration.

Take an aliquot which will give approximately 60–80 mg. of ignited Al_2O_3, or

for 12% alloys use .25 gm. actual sample = 12.5-ml. aliquot;
for 10% alloys use .40 gm. actual sample = 20-ml. aliquot;
for 8–2% alloys use .50 gm. actual sample = 25-ml. aliquot.

In no case use more than .6 gm. of actual sample, even for very low alloys. Add 25 ml. of cold saturated NH_4Cl and 5 ml. of methyl red indicator, heat to a boil and carefully add dilute NH_4OH until just neutral. Immediately filter the precipitated $Al(OH)_3$ on a 11 cm. No. 40 Whatman filter paper (or equal grade) and wash once with warm 2% NH_4Cl solution; do not police the beaker. Carefully wash the precipitate over the edge of the funnel into the original beaker. Care must be taken not to puncture the filter paper, and it is best to start the stream off the paper and not break it while on the paper. This treatment makes it unnecessary to wash the paper with acid in order to reprecipitate the aluminum. Add 10–15 ml. of dilute HCl [21] washing down the sides of the beaker well with the acid. Heat to a boil and reprecipitate as before, adding 15 cc. of saturated NH_4Cl solution. Then filter through the same paper, wash, and police the beaker well [22] several times with warm 2% NH_4Cl solution.[23] Follow with a wash or two of water. Allow the precipitate to drain well, transfer to tared crucibles with covers, and ignited at 950–1,000° C. for an hour or more. Keep the covers on except when in the muffle, where an electric muffle is used. If convenient to use higher temperature, such as those attained with a blast lamp, 1,200° C. is desirable, but great care must be taken during ignition.

Weigh the Al_2O_3 as rapidly and accurately as possible with the covers on the crucibles. A good balance and weights are necessary as the precipitate is small.

$$\frac{\text{gm. } Al_2O_3 \times .529 \times 100}{\text{sample weight}} = \%\ Al$$

[20] This residue may be copper, silicon or other reduced metals. If much silicon is present in the alloys it must be removed before the aluminum can be determined gravimetrically. This can best be done by dehydration with sulfuric acid and removal by filtration, washing very thoroughly. Then make the sample to volume and proceed with the regular analysis.

[21] This amount of acid may not dissolve all the $Al(OH)_3$ precipitate, which may have precipitated in a form which will require a large excess of acid to dissolve. The $Mg(OH)_2$ which might be occluded and is the reason for the double precipitation will dissolve very readily even in a slightly acid solution.

[22] The $Al(OH)_3$ precipitate will stick to the beaker very tenaciously and will require considerable policing, this to be done with a rubber-tipped policeman. A procedure which is convenient is to wash the beaker as well as possible and then wash the sides down with a few ml. of dilute HCl and reprecipitate this as before. The volume of the solution in this case can be kept low enough so that all of the precipitate can be poured into the funnel and washed at once.

[23] Chloride ion is necessary for filtration of $Al(OH)_3$, otherwise the filtration will become very slow and the aluminum precipitate will go back into solution. The chloride, if reasonably low, will burn off upon ignition and cause no trouble.

MANGANESE

Manganese is used as an alloying ingredient in practically all magnesium alloys, the amounts varying from 0.1% to 2%.

The bismuthate method is used entirely with satisfactory results.

Solutions.—(1) N/10 $FeSO_4$ (approx.): Weigh 28–29 gm. of $FeSO_4 \cdot 7H_2O$ crystals and dissolve. Transfer to a liter volumetric flask, add 25 ml. of conc. H_2SO_4 and make to volume. Allow to stand overnight. This solution must be standardized each time before use. To standardize take a 25-ml. aliquot, add 5 ml. of 1 : 1 H_3PO_4, and titrated with N/10 $KMnO_4$ to the pink endpoint.

$$N\ (FeSO_4) = \frac{\text{ml. N/10 } KMnO_4}{25}$$

(2) 1 : 1 H_3PO_4: One part water to one part 85% H_3PO_4.

(3) N/10 $KMnO_4$: Regular standard solution.

Procedure.—Weigh accurately a pair of samples—

for .6–2% Mn use 1 gm.;
for .1–.6% Mn use 3 gm.

Dissolve in 1 : 4 H_2SO_4 and when solution is complete add 8–10 ml. of conc. HNO_3 (avoid a large excess) to dissolve the dark residue. Boil for two minutes, cool, add ½ gm. of sodium bismuthate, and allow to stand for 3–5 minutes with frequent stirring. Filter through an asbestos pad [24] with the aid of suction. The filtrate should be clear; if not, refilter.

Immediately titrate the filtrate with N/10 $FeSO_4$, adding 5 ml. of 1 : 1 H_3PO_4 at the endpoint when the color has practically faded out. Continue the titration until colorless, add 1 ml. in excess and back-titrate with N/10 $KMnO_4$ to the pink endpoint.

$$\frac{\text{ml. net N/10 } FeSO_4 \times .0011 \times 100}{\text{sample weight}} = \%\ \text{Mn}$$

ZINC

Zinc has become one of the important ingredients in magnesium alloys. It is usually present in amounts up to 3%.

For zinc the titration with potassium ferrocyanide is the standard method used. Many elements will interfere, thus making a separation necessary in practically all cases. The separation of cadmium is difficult, depending upon the separation as sulfide at different acid concentrations. Even in the case where only magnesium is present, it is necessary to carry out the sulfide separation before actual determination.

Several methods of titration have been tried with various indicators, both internal and external. The best indicator, we have found, is diphenyl benzidine

[24] Do not use paper to filter off the excess bismuthate, since it will reduce a small amount of the permanganate. A good asbestos pad will filter quite well and rapidly. If it is made up in a Büchner funnel, several filtrations can be made through the same pad. Since chloride reduces permanganate, the asbestos used must be chloride-free.

(Cone and Cady, J. Am. Chem. Soc., **49**, 356–60 (1927)), an internal indicator which gives a good endpoint. The titration must be made slowly.

Standard Solutions.—(1) $ZnCl_2$: Weigh very accurately 4–5 gm. of pure Zn and dissolve in HCl. Dilute to one liter at 20° C. and calculate the Zn equivalent per ml. Use 20 ml. for the titration to standardize the $K_4Fe(CN)_6$ solution.

(2) $K_4Fe(CN)_6$: Dissolve 17–20 gm. of the crystalline potassium ferrocyanide per liter. Allow to stand for three weeks or more: for immediate use .3 gm. of the ferricyanide ($K_3Fe(CN)_6$) per liter can be added, but such a solution gradually changes strength. Standardize as gm. Zn equivalent per ml. against the standard Zn solution.

Indicator.—Diphenyl benzidine: 1 gm. per 100 ml. of conc. H_2SO_4.

Procedure.—Weigh accurately a suitable sample into a 400-ml. beaker (up to 2.5% Zn use 5 gm. sample; for 2.5–3.5% Zn use 2.5 gm. sample). Dissolve in 1–10 H_2SO_4 and dilute to 250 ml.[25] Neutralize slowly with 30% NaOH until a very slight precipitate of $Mg(OH)_2$ remains. (The proper acidity can be obtained more easily by neutralizing until the $Mg(OH_2)$ dissolves very slowly, and then adding 3 gm. of sodium acetate.) The solution should be neutral to methyl orange. Cool, and pass in a rapid stream (8 bubbles per second) of H_2S for 20–30 minutes. Add 10 ml. of filter paper pulp and filter through a rententive paper such as a Whatman 42 or a No. 2. Wash twice with warm water, discarding the filtrate. Dissolve from the paper with 20 ml. of hot 1 : 4 HCl. Wash the paper several times with hot water or to a volume of 150 ml. Boil out the H_2S (test with lead acetate paper), cool, add 10 gm. of NH_4Cl, and neutralize just to the litmus endpoint with 1 : 4 NH_4OH. Add 15 ml. of 1 : 4 H_2SO_4. At this time there should be a volume of 200 ml. and the temperature should be that of the room. Add a small crystal of $K_3Fe(CN)_6$ and 5–6 drops of freshly prepared diphenyl benzidine indicator. Allow to stand until the bluish purple color develops. Titrate with the standardized $K_4Fe(CN)_6$ solution. The titration must be made slowly: near the endpoint the solution will develop a bright purple color and the endpoint comes when one drop changes the color of the solution from the purple to a very light pea-green which holds for several minutes.

$$\frac{\text{ml. } K_4Fe(CN)_6 \times F^* \times 100}{\text{sample weight}} = \% \text{ Zn}$$

F^* = Zn equivalent per ml.

SILICON

Silicon has become an important alloying ingredient in casting alloys. They contain up to .5% Si, and in the case of experimental samples even higher.

Sulfuric acid is the most satisfactory dehydrating agent.

The perchloric acid dehydration is useful, particularly for the lower Si contents, as in pure Mg, or in alloys where it is not an added ingredient. It is not necessary to take to dryness when using this acid. While the price is

[25] When copper and cadmium are present they must be removed. If cadmium is absent, use the electrolyte from the copper determination (see copper). The filtrate from the cadmium separation (see cadmium) can be used for the zinc determination if cadmium is present.

swirl until clear. Add phenolphthalein indicator and 200 ml. of water; titrate until neutral with normal HCl, make to about 500 ml., and mix well.

(2) .1 N $Na_2S_2O_3$.

Procedure.—Weigh out a pair of samples of approximately 5 gm. each. Dissolve in H_2SO_4 and filter the precipitate of metallic copper as soon as the solution is completed. Do not start the determination unless the copper can be filtered off as soon as the sample is in solution. (Note next paragraph.)

With cadmium present in amounts less than 2%, there is little danger of metallic cadmium being filtered off with the copper. When over 2%, cadmium is thrown out to a great extent, and for exact work the electrolytic method should be used. A suitable excess of acid and intermittent stirring for 15 minutes will dissolve all but traces of cadmium from the spongy black or red copper precipitate. Where copper is very low a strip of aluminum foil added near the end assists in getting a complete separation of the copper. Wash the copper and transfer as much as possible back to the original beakers. Run hot 1 : 1 HNO_3 through the paper and dissolve all the copper by boiling, adding more acid if necessary. Tin, if present, may be removed at this point by boiling down almost to dryness after adding more HNO_3, diluting back, and filtering off metastannic acid.

Boil the HNO_3 solution about three minutes, cool a little, and make alkaline with ammonia as shown by the deep blue color; then boil for three minutes. Now make acid with acetic acid, add 5 ml. excess glacial acetic acid, then boil two or three minutes. The volume should be 60 to 100 ml. Cool to room temperature, add 3–5 gm. of KI, and titrate in about three minutes with .1 N $Na_2S_2O_3$ solution, using starch solution indicator at the finish.

$$\frac{\text{ml. .1 N } Na_2S_2O_3 \times .00636 \times 100}{\text{sample weight}} = \% \text{ copper}$$

CADMIUM

Cadmium is sometimes alloyed with magnesium, but seldom to exceed 2%. There are two methods used for analysis, the electrolytic and the iodide. In both cases the same elements, viz. copper and zinc, will interfere, and the same separations must be made.

The most satisfactory method for the removal of copper is by electrolysis in acid solution; but it can also be removed with H_2S in a strongly acid solution.

The separation of cadmium and zinc is quite difficult, depending upon the separation with H_2S at different acid concentrations. If the acidity is too high, the cadmium will not precipitate completely, and if too low zinc will be carried down. The magnesium which is present makes a good indicator in this case. In neutralizing the solution, when the $Mg(OH)_2$ will dissolve readily in 15 minutes with a slight amount of stirring, the cadmium will precipitate without the zinc. A strong caustic solution gives the best form of $Mg(OH)_2$ for this purpose.

Separation of Zinc

Solutions.—(1) Strong NaOH. 45–48%, from C.P. NaOH.

(2) H_2S. Any good source.

Procedure.—This procedure is not effective if HCl is used. For alloys up to 2% weigh 5 gm. of sample accurately; for higher percentages use proportion-

ate samples, but none to contain more than .1 gm. cadmium. Dissolve in 12 ml. of conc. H_2SO_4 and remove the copper electrolytically,[29] as outlined under that method. *Partially neutralize with strong NaOH until the chunky $Mg(OH)_2$ precipitate formed will just readily and completely dissolve with slight stirring in 15 minutes. Pass in a slow stream of H_2S* (one bubble per second) *for 5 to 10 minutes* or until the cadmium is precipitated. *It is best to* avoid using an excess of H_2S because the zinc might be precipitated and determined as cadmium. Filter through a No. 42 Whatman paper (11-cm.) and test for complete precipitation of the cadmium by adding several drops of NaOH and 10 ml. of H_2S water. If a yellow color appears, return everything to the original beaker and wash the paper well. Pass in a slightly more rapid stream of H_2S. Add a few ml. of paper pulp and filter. Wash the precipitate twice with hot water, filling the paper completely full and allowing it to drain completely each time.[30]

Electrolytic Method

Solution.—(1) 10% KCN. 10 gm. in 90 ml. of water.

Procedure.—Dissolve the precipitate of cadmium in HCl and add 5 ml. conc. H_2SO_4, boil to fumes and transfer to an electrolytic beaker. Add 2 drops of phenolphthalein indicator and NaOH until distinctly alkaline (red color). $Cd(OH)_2$ will precipitate. Add 10% KCN solution until the precipitate just dissolves.

The electrodes to be used are platinum gauze electrodes of the rotating type, and should be clean and bright when used. If they are not, they should be dipped into a 1 : 1 HNO_3 solution and the acid washed off well. Place the electrodes in position so that when the anode is rotated it will not strike the cathode. Raise the solution to be electrolyzed so that it just covers the electrodes, increasing the volume if necessary. Rotate the anode so that there is slight (not rapid) movement throughout the solution.

Electrolyze for 30 minutes with a current of .6 amperes per electrode, then raise to 1.2 amperes per electrode for another 30 minutes. Lower the electrolytic beaker, and wash it well with hot water without breaking the current. Remove the electrodes completely from the solution, breaking the current, and wash them by dipping in three successive beakers of hot water. Allow to drain well and then rinse well with 95% alcohol to remove the water. Drain well and dry in the 100° C. oven for a few minutes. Allow to cool in a desiccator and weigh as soon as possible. (Platinum will cool very rapidly.) Dissolve the cadmium plate in 1 : 1 H_2SO_4, wash off the acid and rinse as previously, dry and weigh.

(Weight of electrode + plate) − (weight of electrode) = grams of cadmium

$$\frac{\text{gm. cadmium} \times 100}{\text{sample weight}} = \%\ \text{cadmium}$$

Iodine Method

Solutions.—(1) N/10 I_2. Regular standard solution.

(2) N/10 $Na_2S_2O_3$. Regular standard solution.

[29] Where copper has been determined, the electrolyte from that test can be used for cadmium.

[30] Save the filtrate and washings for the zinc determination, when Zn is present.

(3) Starch indicator. See iodide method for Cu.

Procedure.—After filtering off the CdS, as given under "Separation of Zinc," transfer the paper and precipitate to the original beakers, add 50 ml. of water, and stir to break up the paper and precipitate. Add 20.00 ml. of $N/10\ I_2$,[31] or an excess, and 10 ml. of conc. HCl. Stir until all the CdS has reacted and titrate back with $N/10\ Na_2S_2O_3$ to the colorless starch endpoint; then back-titrate with $N/10\ I_2$ to a distinct blue.

$$\frac{\text{Net ml. } N/10\ I_2 \times .0056 \times 100}{\text{sample weight}} = \%\ \text{cadmium}$$

IRON

There are no alloys of magnesium and iron, so this analysis has to deal with iron only as a small impurity. One of the standard methods can usually be used, the choice depending on what elements are present. If aluminum is present, it is impossible to precipitate and filter off the iron; if aluminum is absent, and if there is no appreciable amount of copper or tin present, it is more accurate to precipitate and titrate with titanous chloride. In the case of the aluminum alloys it is most practical to dissolve the metal and titrate with either dichromate or permanganate without separation.

Permanganate Method

Solutions.—(1) 1 : 4 H_2SO_4. One part conc. H_2SO_4 to 4 parts of water.

(2) 1 : 1 H_3PO_4. One part 85% H_3PO_4 to one part of water.

(3) $N/50\ KMnO_4$. 50 ml. of $N/10\ KMnO_4$ diluted to 250 ml. and standardized against Bur. of Standards sodium oxalate.

Procedure.—Weigh a 5-gm. sample, dissolve it in 1 : 4 H_2SO_4 in a 400-ml. beaker, dilute to 250 ml. and cool. Add 5 ml. of 1 : 1 H_3PO_4 and titrate to a light pink endpoint. Run a blank, using the same volume of water and reagents, and deduct this from the titration.

$$\frac{\text{Net ml. } KMnO_4 \times .001117 \times 100}{\text{sample weight}} = \%\ \text{iron}$$

NICKEL

Nickel is seldom used for alloying, except in a few special cases where the nickel is as high as 50% or more. As an impurity it is very important, since extremely small amounts will give the magnesium metal definite characteristics.

The method to be used is the standard dimethylgloxime method. Very few elements interfere, but it is preferable to have large amounts of copper, iron,

[31] The standard procedure is to add about 250 ml. of water and a moderate amount of dilute HCl to the macerated CdS precipitate and paper. Then add the excess iodine and proceed with the regular titration. As a method which would probably work equally well it is possible to acidify the iodine with N/1 HCl before adding it. However, the method as outlined gives satisfactory results in these cases, because the cadmium is usually low (below 2%) and the CdS precipitate does not readily react until the acid is added.

lead and cobalt absent; these are usually not encountered in any high percentage in magnesium alloys, and usually no separations are made preliminary to the determination.

Dimethylgloxime Method

Solutions.—(1) NH_4Cl. Saturated solution.

(2) Dimethylgloxime. Approximately a 1% sol. in 1 : 1 ethyl alcohol.

(3) NH_4OH. 1 : 4 solution.

Procedure.—For alloys containing up to .6% of nickel, weigh 5-gm. samples and dissolve in HNO_3. For higher alloys use proportionate samples, but none to contain more than .04 gm. of nickel. For high nickel alloys it will be necessary to make a sample to volume and use an aliquot. The solution should have a volume of 200 ml., and preferably be free from copper and lead (if these metals are present, remove by electrolysis). Add 30 ml. of NH_4Cl solution and sufficient tartaric or citric acid to keep the iron and aluminum in solution. Neutralize with NH_4OH and if any precipitate forms add more NH_4Cl or tartaric acid, whichever is needed. Make just acid, warm to 70° C., and add 25 ml. of dimethylgloxime. Neutralize to litmus and add a slight excess of NH_4OH. If the precipitate is large, allow to settle for one-half hour, and if same is small, overnight. Filter through a tared Gooch crucible and wash with hot water several times. Dry for one hour at 100° C. and weigh.

$$\frac{\text{Weight precipitate} \times .2032 \times 100}{\text{sample weight}} = \%\ \text{nickel}$$

TIN

In experimental alloys it is sometimes necessary to analyze for tin; at present there are no commercial magnesium alloys containing it.

The determination, either volumetrically or gravimetrically, is quite simple. The volumetric method is to be preferred because the precipitate of metastannic acid which is filtered off in the gravimetric determination is practically always contaminated with whatever salts that are present. In the volumetric determination any metal which will remain in a reduced state after solution and use up iodine upon titration will interfere. Also very large amounts of copper or anything which makes the endpoint difficult to detect should be absent. Usually no interfering elements are present.

CALCIUM

It is only recently that calcium alloys have been produced; previously the metal had been present only as a small impurity. The alloy contains varying amounts of calcium, but generally it is present at around 80%.

There are two methods of analysis available, the potentiometric and the volumetric. The method to be used depends upon the amounts and kinds of impurities present, and the conditions. The potentiometric method is the most rapid and usually is used unless a very accurate analysis is desired or if there are special separations to be made. In those cases the volumetric method, using N/10 $KMnO_4$, is used.

For the determination of calcium as a small impurity in magnesium alloys or metal, it is necessary to remove the interfering elements and most of the magnesium before the determination is made by the usual method.

Potentiometric Method

Solutions.—(1) N/1 NaOH. Regular Standard solution.

(2) N/1 Na_2CO_3. Regular standard solution.

Procedure.—Weigh accurately a 2-gm. sample (for routine analysis the calculation can be much simplified if exactly .2-gm. samples are titrated; for accurate work a sample should be chosen so that a 10-ml. titration of N/1 Na_2CO_3 is obtained). Add carefully 25 ml. of water and when the violent reaction is over add 10 ml. of conc. HCl, or enough to clear the solution. Make to 100 ml. volume and take a 10-ml. aliquot (for a larger titration, when needed, use a larger aliquot). Neutralize with N/1 NaOH to the methyl red endpoint. Heat the solution to boiling and titrate the magnesium potentiometrically with N/1 NaOH.

$$\frac{\text{ml. N/1 NaOH} \times .0122 \times 100}{\text{sample weight}} = \%\ \text{magnesium}$$

Immediately following the magnesium titration, titrate the calcium potentiometrically, increasing the heat and speed of the stirrer slightly.

$$\frac{\text{ml. N/1 } Na_2CO_3 \times .020 \times 100}{\text{sample weight}} = \%\ \text{calcium}$$

If exactly .2 gm. of sample is titrated, the calculation becomes: ml. N/1 $Na_2CO_3 \times 10 = \%$ calcium.

Volumetric Method

Solutions.—(1) NH_4Cl. Saturated solution.

(2) NH_4OH (1 : 4). One part of conc. NH_4OH to four parts of water.

(3) $(NH_4)_2HPO_4$. 15% solution. 15 gm. of the salt dissolved in 85 ml. of water.

(4) NH_4OH (1 : 10). One part conc. NH_4OH to ten parts of water.

(5) H_2SO_4 (1 : 4). One part conc. H_2SO_4 to four parts of water.

(6) HCl (1 : 4). One part conc. HCl to four parts of water.

Procedure.—Weigh 2-gm. samples accurately. Dissolve in 25 ml. of water, adding 10 ml. of conc. HCl and 5 ml. HNO_3 when the violet reaction has subsided. The solution should be clear. Heat to boiling and cool. Make the sample to 500 ml. and take a 20-ml. aliquot. Add 20 ml. of NH_4Cl solution and precipitate the iron and aluminum by making the solution slightly alkaline to methyl red with 1 : 4 NH_4OH. Filter and wash well. If the precipitate is large it is well to dissolve this precipitate and reprecipitate. Heat the filtrate to boiling and slowly add 20 ml. of ammonium oxalate solution with stirring, bring back to a boil while stirring and allow it to settle for 20 minutes. Filter the precipitate through a No. 42 Whatman (or equal grade) paper and wash with hot water twice. Wash the oxalate precipitate over the sides of the funnel into the original beakers and dissolve in 1 : 4 HCl, reprecipitate, filter through the original paper and wash with hot water until chloride- and oxalate-free.

Puncture the paper and wash the precipitate through into the original beaker, saving the paper. Add 15 ml. 1 : 4 H_2SO_4 and heat to 80° C. and titrate with N/10 $KMnO_4$, using the torn up paper, adding it just as the endpoint is reached. Continue the titration to the light pink endpoint.

$$\frac{\text{ml. N/10 KMnO}_4 \times .0020 \times 100}{\text{sample weight}} = \% \text{ calcium}$$

Acidify the filtrate from the calcium determination, and heat to about 70° C. Add 15 ml. of 15% $(NH_4)_2HPO_4$ solution. Neutralize with 1 : 4 NH_4OH to litmus paper and then add conc. NH_4OH equal to 1/9 of the final volume of the solution while stirring well (do not hit the sides of the beaker with the stirring rod). Allow to set at least 2 hours and filter through No. 42 Whatman (or equal grade) paper. Wash with cold 1 : 10 NH_4OH, completely filling the funnel and allowing to drain completely each time. Drain well, fold papers, transfer to tared crucibles, and place in front of the muffle until dried, and the papers are burned off completely. Ignite at 950° C. The precipitate should be white; if not, break up with a platinum wire and reignite. Cool in a desiccator and weigh the $Mg_2P_2O_7$.

$$\frac{\text{gm. Mg}_2\text{P}_2\text{O}_7 \times .2184 \times 100}{\text{sample weight}} = \% \text{ magnesium}$$

Calcium as a Small Impurity

Solutions.—(1) N/1 NaOH. 40 gm. per liter. (Approx.)

(2) NH_4Cl. Saturated solution.

(3) $(NH_4)_2C_2O_4$. Saturated solution.

(4) NH_4OH (1 : 4). One part conc. NH_4OH to four parts of water.

(5) H_2SO_4 (1 : 4). One part conc. H_2SO_4 to four parts of water.

(6) $KMnO_4$, N/10. Regular standard solution.

Procedure.—Weight accurately a 5-gm. sample into a 400-ml. beaker, add 50 ml. of water and dissolve with a slight excess of conc. HCl, transfer to a 500-ml. volumetric flask. Neutralize with approximately N/1 NaOH to the methyl red endpoint, and add about 5 g. of ordinary sugar. Calculate the amount of approximate N/1 NaOH required to precipitate the sample if it were pure magnesium. Add 95% of the calculated amount, make to volume and mix well. Filter through a good qualitative paper into a dry graduated cylinder, discarding the first 25 ml. of filtrate. Transfer 300 ml. of the filtrate into a beaker, acidify, add 25 ml. of NH_4Cl solution. Heat to boiling, neutralize with 1 : 4 NH_4OH, and slowly add 20 ml. of $(NH_4)_2C_2O_4$ solution while stirring. Allow to settle 20 minutes and filter through a No. 42 Whatman (or equal grade) paper. Wash with hot water until chloride- and oxalate-free. Puncture the paper, washing the precipitate through into the original beaker. Save the paper. Add 15 ml. of 1 : 4 H_2SO_4 and heat to 80° C. Titrate with N/10 $KMnO_4$, tearing up the paper and adding it as the endpoint is reached. Continue the titration to the light pink endpoint.

$$\frac{\text{ml. N/10 KMnO}_4 \times .0020 \times 100}{3/5 \text{ of sample wt.}} = \% \text{ calcium}$$

NOTE.—In the case of alloys containing zinc, etc., the interfering elements must be removed. This can best be accomplished by the addition of a calculated excess of standard Na_2S as in rapid method (see below), and a correction made on NaOH to add.

LEAD

Recently lead has been used in a few experimental alloys. These contain about 4% of lead.

There are three methods available for this determination, the electrolytic and precipitation of the lead as either sulfate or chromate. The electrolytic is the preferred method, and thus far the chromate method has not been used for alloys. See the Chapter on Lead, p. 500.

RAPID METHOD FOR DETERMINATION OF TOTAL MAGNESIUM IN MAGNESIUM ALLOYS

In the marketing of certain magnesium alloy scrap, it is necessary to have a control method to indicate when the material meets the guarantee for per cent total Mg. Two general methods are available for this, namely a potentiometric titration, or a modification of the rapid method for determination of magnesium oxide in dolomitic limestone.

The first method tried was the potentiometric titration, but the results were low and not consistent. In the rapid limestone method the results were found to be more consistent, and this method is used. Magnesium is determined by this method by determining the amount of NaOH necessary to precipitate it. In our case, the aluminum will interfere, as well as such metals as copper, zinc, cadmium, manganese and tin. In order to prevent this interference, a solution of Na_2S is added to precipitate the interfering metals.

LIME METHOD

Solutions.—(1) 30% NaOH. 30 gm. C.P. NaOH dissolved in 70 ml. of water.

(2) Na_2S solution. Dissolve one gm. $Na_2S \cdot 9H_2O$ in 100 ml. of water. 10 ml. of this solution should be titrated with N/1 HCl to determine its acid equivalent.

Procedure.—Weigh a sample of between .4 and .5 gm. of the alloy and add 25 ml. of water. Dissolve with 5 ml. of conc. HCl. Transfer to a 250-ml. volumetric flask and add 10 ml. of aqueous methyl red indicator. Add dropwise, from a pipette, a solution of 30% NaOH with vigorous shaking between each addition until the aluminum has been precipitated, but allow a good red color to remain. Stopper the flask and shake violently for 3 minutes. Continue

the neutralization with N/1 NaOH, shaking violently between each small addition, to the yellow endpoint. Add 10 ml. of the Na_2S solution and shake well. Neutralize with N/1 HCl, but leave slightly on the alkaline side; this should not require as much as the acid equivalent of the Na_2S added. Run in from a burette 50 ml. of N/1 NaOH and make to volume. Shake well and filter through a fluted filter paper, using a dry funnel and beaker. Discard the first 25 ml. of solution. Pipette a 25-ml. aliquot of the filtered solution into a flask and titrate with N/10 HCl to the methyl red endpoint. The difference between the N/1 NaOH and the N/10 HCl used for back-titration is equivalent to the N/1 NaOH used to precipitate the magnesium. The per cent magnesium is calculated as

$$\frac{(\text{ml. N/1 NaOH} - \text{ml. N/10 HCl}) \times .0122 \times 100}{\text{sample weight}} = \%\ \text{magnesium}$$

MANGANESE [1]

Mn, *at.wt.* 54.93; *sp.gr.* 7.2; *m.p.* 1260°; *b.p.* 1900° C.; *oxides*, MnO, Mn_2O_3 Mn_3O_4 (*ignition in air*), MnO_2, MnO_3, Mn_2O_7

Manganese occurs associated with iron in many rocks. As oxide it is found in sandstones and limestones, especially in rocks high in iron. In these the percentage seldom exceeds 0.5%. The more important minerals are:—pyrolusite, black oxide of manganese, MnO_2, the chief source; manganite, $Mn_2O_3 \cdot H_2O$; psilomelane, a hydrous manganese manganate; rhodochrosite, $MnCO_3$; rhodenite, $MnSiO_3$ and spessartite, $Mn_3Al_2(SiO_4)_3$.

DETECTION

General Procedure.—In the usual course of analysis manganese is found in the filtrate from the hydroxides of iron, aluminum and chromium, the previous groups having been removed with hydrochloric acid, hydrogen sulfide and ammonium hydroxide in the presence of ammonium chloride. Manganese, cobalt, nickel and zinc are precipitated as sulfides in an ammoniacal solution. The sulfides of manganese and zinc are dissolved by cold dilute hydrochloric acid, H_2S expelled by boiling and manganese precipitated as the hydroxide by addition of potassium hydroxide in sufficient amount to dissolve the zinc (sodium zincate). Manganese is now confirmed by dissolving this precipitate in nitric acid and adding a strong oxidizing agent such as sodium bismuthate, red lead or lead peroxide to the conc. nitric acid solution. A violet-colored solution is produced in presence of manganese. Chlorides should be absent.

Manganese in soils, minerals, vegetables, etc., is detected by incinerating substances, treating with nitric acid, and adding perchloric acid, and the solution is evaporated to strong fumes of $HClO_4$ to destroy organic matter. HNO_3 (sp.gr. 1.135) is added, the solution is boiled to expel free chlorine, followed by the addition of ammonium persulfate, silver nitrate, and boiling, etc. A pink color is produced in the presence of manganese.

[1] Manganese compounds were thought to be those of iron until Scheele (1774) proved these to be distinct. The metal is used largely in alloys of iron—speigeleisen, ferro-manganese, manganese steel. Manganese bronze is an alloy of manganese and copper; manganin, an alloy of copper, nickel and manganese. In the analysis of manganese compounds, volumetric methods take advantage of the varying valences of the element (See oxides above). Certain compounds are valuable analytical reagents.

Manganese compounds heated with borax in the oxidizing flame produce an amethyst red color. The color is destroyed in the reducing flame.

Fused with sodium carbonate and nitrate on a platinum foil manganese compounds produce a green-colored fusion (" robin egg blue ").

ESTIMATION

The bismuthate method is now considered to be the most accurate method for manganese in high grade manganese ores, ferro-manganese, and manganese metal. The gravimetric method is of interest in connection with special problems. Very small quantities of manganese are best estimated colorimetrically after the manganese has been converted into permanganic acid.

Speigeleisen or ferromanganese is an important alloy for the steel industry. The element is determined in certain paint pigments—green and violet manganous oxides, in dryers of oils, etc. It occurs in a number of alloys.

In analyses, manganese passes into the filtrate from the double ammonia precipitation and is in part precipitated with calcium and the remainder as manganese ammonium phosphate with magnesium, unless provision is made for its separation and estimation.

PREPARATION AND SOLUTION OF THE SAMPLE

In dissolving the sample the following facts will be recalled: The metal dissolves in dilute acids, forming manganese salts. The oxides and hydroxides of manganese are soluble in hot hydrochloric acid. Manganous oxide is soluble in nitric or in sulfuric acid; the dioxide is insoluble in dilute or concentrated nitric acid, but is soluble in hot concentrated sulfuric acid.

Ores of Manganese.—A sample of powdered ore weighing 1 gram is brought into solution by digesting with 25 to 50 ml. of hydrochloric acid (1.19) for fifteen to thirty minutes on the steam bath. If much silica is present 5 to 10 ml. hydrofluoric acid will assist solution. Five ml. of sulfuric acid are added and the mixture evaporated and heated until fumes of sulfur trioxide are evolved. The residue is taken up with a little water and warmed until the sulfates have dissolved. If decomposition is incomplete and a colored residue remains, this is filtered off, ignited in a platinum dish and fused with a little potassium bisulfate. The fusion is dissolved in water containing a little nitric acid and the solution added to the bulk of the sample.

Sulfide Ores—Pyrites, etc.—The sample may be treated with HNO_3 and evaporated with $HClO_4$; the residue is taken up with HNO_3 (sp.gr. 1.135), the solution is boiled to expel free chlorine and the determination completed by the bismuthate method.

Slags.—These may best be decomposed by treating with HNO_3 (sp.gr. 1.135) plus a few drops of HF and evaporation with $HClO_4$. The determination is completed as described in the preceding paragraph.

Iron Ores.—May be treated in the same fashion as slags (preceding paragraph).

Alloys. Manganese Alloys.—One gram of ferromanganese is dissolved in 50 ml. of dilute nitric acid (sp.gr. 1.135) and treated with sodium bismuthate and the solution heated to boiling. The solution is cleared with H_2SO_3, cooled and diluted to 500 ml. and 10 to 25 ml. is treated with about 30 ml. of dilute nitric acid and manganese determined by the bismuthate method.

Manganese Bronze.—The sample may be dissolved in HNO_3 (sp.gr. 1.135) and the determination of manganese made by the bismuthate method.

Ferro-titanium Alloy.—This is best decomposed by fusion with sodium peroxide in a pure iron crucible, the fusion is taken up in water and rendered slightly acid with HNO_3. Sufficient HNO_3 (sp.gr. 1.42) is added to give a specific gravity of 1.135. The determination is completed by the bismuthate method.

Manganese in Ferro-chrome and Metallic Chromium.—Fuse one or two grams of the 40-mesh sample of low carbon ferro-chromium or of the 100-mesh high carbon ferrochromium in a pure iron crucible with 8 to 12 grams of Na_2O_2, dissolve the melt in water, filter and wash the residue with water. The iron residue containing the manganese is dissolved in nitric acid (sp.gr. 1.135) and the determination completed by the sodium bismuthate method.

For the determination of manganese in silico-manganese and manganese-silicon, the sample is dissolved in platinum in HF and HNO_3 and the solution evaporated to several ml. The residue is taken up with HNO_3 (sp.gr. 1.135) containing 1.25 grams of boric acid, the solution digested for ten minutes at approximately 80° C., transferred to an Erlenmeyer flask and the determination completed by the bismuthate method.

Ferro-aluminum.—The method used for steel is suitable for this substance.

Vanadium Alloys.—For vanadium alloy, fuse the sample cautiously with Na_2O_2 in a pure iron crucible, dissolving the melt in water, add a little Na_2O_2, boil for three minutes and filter. The residue is dissolved in HNO_3 (sp.gr. 1.135) plus a small amount of H_2SO_3 and the determination completed by the bismuthate method.

Molybdenum Alloys.—The manganese in these alloys may be determined in the same way as in steels.

Tungsten Alloys and Ferrotungsten.—Dissolve the sample in HF and a little HNO_3 in a platinum dish, add $HClO_4$ and evaporate to fumes of $HClO_4$. Transfer to a 250-ml. beaker with 100 ml. of water, boil to expel free chlorine, filter and wash with 1% HNO_3. Add sufficient HNO_3 (sp.gr. 1.42) to give a nitric acid solution of 1.135 specific gravity and finish by the bismuthate method. The tungstic acid residue may be tested by treating with a 5% excess of 10% NaOH solution and a little Na_2O_2, boiling and filtering. Any residue is dissolved in HNO_3 (sp.gr. 1.135) plus a little H_2SO_3, and added to the main solution. Complete the determination by the bismuthate method.

Ferro-Silicon.—Dissolve the sample in HF and HNO_3 and add either H_2SO_4 or $HClO_4$ and evaporate to fumes of sulfur trioxide or of $HClO_4$, take

up with HNO_3 (sp.gr. 1.135), boil in case $HClO_4$ was used and complete by the bismuthate method.

Iron and Steel.—0.5 to 1 gram of steel is dissolved by heating with 30 to 50 ml. of dilute nitric acid (1.135). The volumetric method by oxidation with sodium bismuthate is generally recommended, no separations of other substances being required, as manganese may be determined directly in the sample.

Manganese in high carbon iron and steel is best worked by solution in HNO_3 (sp.gr. 1.135) and giving a preliminary oxidation with ammonium persulfate to destroy the carbon, followed by cooling, and completing by the bismuthate method.

Pig and Cast Iron.—One gram of the drillings is dissolved in 30 ml. of dilute nitric acid (1.135 sp.gr.), and as soon as the action has ceased the sample is filtered through a 7-cm. filter and the residue washed with 30 ml. more of the acid. The filtrate containing the manganese is now treated according to the procedure for steel.

MATERIALS INSOLUBLE IN ACID

Silico-Manganese, Ferro-Chrome, Ferro-Tungsten.—These alloys are best decomposed by fusion with sodium carbonate and magnesium oxide, in proportion of 2 parts Na_2CO_3 and 1 part MgO. The fused mass is broken down in a mortar with water, the paste transferred to a beaker and then water added to make the solution to about 150 ml. Sodium peroxide is added and the solution boiled. The precipitate MnO_2 is allowed to settle and is then washed by decantation. The residue may contain impurities such as SiO_2, etc., from which separations may be necessary.

SEPARATIONS

This section includes methods of special separations of manganese from elements that may interfere in its determination. As is frequently the case, isolation of manganese is not necessary, since it may be determined volumetrically in presence of a number of elements, which would interfere in its gravimetric determination. The analyst should be sufficiently familiar with the material to avoid needless manipulations, which not only waste time, but frequently lead to inaccurate results.

Removal of Elements of the Hydrogen Sulfide Group.—This separation may be required in the analysis of certain alloys where a separation of manganese from copper is required.

The acid solution containing about 4% of free hydrochloric acid (sp.gr. 1.2), is saturated with hydrogen sulfide and the sulfides filtered off. Manganese passes into the filtrate. This treatment will effect a separation of manganese from mercury, lead, bismuth, cadmium, copper, arsenic, antimony, tin and the less common elements of the group.

Separation of Manganese from the Alkaline Earths and the Alkalies.—The separation is occasionally required in the analysis of clays, limestone, dolomite, etc. It is required in the complete analysis of ores. In the usual course of a complete analysis of a substance, the filtrate from the hydrogen sulfide group is boiled free of H_2S and is treated with a few ml. of nitric acid to oxidize the iron.

The solution is made slightly ammoniacal with ammonia, in presence of ammonium chloride, whereby iron, aluminum and chromium are precipitated as hydroxides. The filtrate is treated with hydrogen sulfide or colorless ammonium sulfide, whereby manganese, nickel, cobalt and zinc are thrown out as sulfides and the alkaline earths and alkalies remain in solution.

Separation of Manganese from Nickel and Cobalt.—The free acid of the sulfate or chloride solution of the elements is neutralized with sodium carbonate and a slight excess added. It is now made strongly acid with acetic acid and 5 grams of ammonium acetate added for every gram of nickel and cobalt present. The solution is now diluted to about 200 ml. and saturated with hydrogen sulfide, whereby nickel and cobalt are precipitated as sulfides and manganese remains in solution.

Separation of Manganese as Manganese Dioxide.—Manganese is precipitated as MnO_2 from acid solution by $KClO_3$, $KBrO_3$ and from alkaline solution by Cl, Br etc. The importance of this separation makes it advisable to place the details of the procedure later in the text under Gravimetric Methods. Reducing agents should be absent. If the precipitate of MnO_2 is large, appreciable amounts of Fe, Co, Sb and V will be occluded. The oxides of W, Si, Cb and Ta will precipitate with MnO_2. See details under the Gravimetric Methods.

Separation of Manganese from Iron and Aluminum, Basic Acetate Method.—The procedure effects a separation of iron, aluminum, titanium, zirconium and vanadium from manganese, zinc, cobalt and nickel.

The separation depends upon the fact that solutions of acetates of iron, aluminum, titanium, zirconium and vanadium are decomposed when heated and the insoluble basic acetates precipitated, whereas the acetates of manganese, zinc, cobalt and nickel remain undecomposed when boiled for a short time.

$$Fe(C_2H_3O_2)_3 + 2HOH = 2HC_2H_3O_2 + Fe(OH)_2 \cdot C_2H_3O_2.$$

The solvent action of the liberated acetic acid is prevented by the addition of sodium acetate which checks ionization of the acid. The method requires care and is somewhat tedious, but the results obtained are excellent.

Procedure.—To the cooled acid solution of the chlorides is added a concentrated aqueous solution of sodium carbonate from a burette with constant stirring until the precipitate that forms dissolves slowly. A dilute solution of the carbonate is now added until a slight permanent opalescence is obtained. With the weak reagent and careful addition of the carbonate drop by drop the proper neutralization of the free acid is obtained. With considerable iron present the solution appears a dark red color, fading to colorless as the quantity of iron decreases to a mere trace in the solution. Three ml. of acetic acid (sp.gr. 1.044) are added to dissolve the slight precipitate. The more perfect the neutralization before heating the less amount of reagent required for precipitating iron—an excess of reagent does no harm. If this does not clear the solution in two minutes, more acetic acid is added a drop at a time until the solution clears, allowing a minute or so for the reaction to take place with each addition. The solution is diluted to about 500 ml. and heated to boiling and 6 ml. of a 30% sodium acetate solution added. The solution is boiled for one minute and removed from the flame. (Longer boiling will form a gelatinous precipitate, difficult to wash and filter.) The precipitate is allowed to settle for a minute

or so[illegible]tered, while the liquid is hot, through a rapid filter and washed with [illegible] sodium acetate solution three times. The apex of the filter is punc[illegible] a glass stirring rod and the precipitate washed into the original beak[illegible]h the precipitation was made with a fine stream of hot, 1 : 1 hydr[illegible]id solution from a wash bottle. (Dilute HNO_3 may be used in place [illegible].

A [illegible]ecipitation with neutralization of the acid and addition of sodium acetat[illegible] exactly as directed above. It is advisable to evaporate the soluti[illegible]l volume to expel most of the free mineral acid before addition of Na_2CO_3 [illegible] large quantities of this reagent. The filtrates contain manganese, [illegible] cobalt and nickel; the precipitate iron, aluminum, titanium, zirconium, [illegible]adium.

GRAVIMETRIC METHODS

SEPARATION OF MANGANESE AS MANGANESE DIOXIDE

Manganese is oxidized to MnO_2 in neutral solution of the manganous salt by chlorine, bromine, hypochlorite, hypobromite, ferricyanide; in acid solution by ammonium or potassium persulfate, potassium bromate or potassium perchlorate. The reaction with bromate follows:

$$5Mn^{++}+2BrO_3^-+4H_2O=5MnO_2+Br_2+8H^+.$$

Iron may be present up to 100 : 1 but in excess of this hinders precipitation. In presence of large amounts of iron precipitation with hydrated zinc sulfate is advisable. A high concentration of ferric iron and a low concentration of manganese favor the formation of permanganate. In presence of iron under definite conditions results are reproducible and an empirical factor has been worked out. The National Bureau of Standards recommends multiplying the theoretical by 1.028. Kolthoff and Sandell apply a slightly lower factor under conditions given below. These authors recommend precipitation of MnO_2 by means of potassium bromate in presence of dilute acid, giving preference to this method over persulfate, since this reagent is not decomposed by boiling as is the persulfate as the precipitation of MnO_2 is more certain in presence of iron. Details of the method follow later.

POTASSIUM BROMATE METHOD FOR DETERMINATION OF MANGANESE [2]

Convenient quantities for the separation range from 20 to 150 mg. of manganese. The method is useful in determining comparatively large amounts of manganese and is specially suited to the evaluation of manganese ores.

[2] Volumetric Determination of Manganese as Dioxide, by I. M. Kolthoff and E. B. Sandell, Ind. Eng. Chem., Anal. Ed. 1, 181, 1929.

The ore is brought into solution preferably by treating the finely ground sample with HCl and $KClO_3$. If iron is not already present an [illegible] about equal to that of the manganese is added in form of ferric nitrate or [illegible]. The presence of this iron makes it possible to get consistent results. [illegible] sulfate may be added in place of iron; a slightly higher empirical factor is then necessary.

Separation of Manganese.—To a volume of about 50 ml., containing 20 to 150 mg. manganese, sufficient dilute sulfuric or nitric acid is added to make the solution 0.8 to 1.0 N with respect to acid. Iron or zinc should be present for consistency of the empirical factor as stated above. One to 2 grams of potassium bromate are then added and the solution is heated to boiling and the boiling continued from 10 to 20 minutes according to the amount of iron present. (Samples containing a large ratio of iron require longer boiling than those in which the ratio is small.) If the iron content is more than 100 : 1 the period of precipitation is increased to such an extent that it is advisable to use the bismuthate method. Water is added to replenish that lost by boiling. The precipitate is filtered through ordinary filter paper, passing the first portion again through the filter if it is turbid. Wash the dioxide thoroughly with hot water, using 6–10 portions of about 10 ml. each. The manganese may now be determined either gravimetrically or volumetrically. If it is determined gravimetrically an ashless filter paper should have been used and the oxide ignited and weighed as Mn_3O_4. The oxide may be dissolved in H_2SO_4, the excess of acid expelled and the residue weighed as $MnSO_4$. The results for Mn should be multiplied by 1.02 if zinc is present and iron absent, or by 1.01 if iron alone is present. (See also under Volumetric Methods for the details that follow at this stage.)

Manganates of zinc or calcium will be precipitated if present in large amounts.

Manganese may also be precipitated by ammonium persulfate in an ammoniacal solution, potassium chlorate and chloride of lime in presence of zinc chloride in a neutral solution.[3]

DETERMINATION OF MANGANESE AS PYROPHOSPHATE

Manganese is precipitated as ammonium manganese phosphate, NH_4MnPO_4, and then ignited to pyrophosphate, $Mn_2P_2O_7$. The method is known as Gibbs' Phosphate Process.[4]

Procedure.—The cold solution of manganese chloride [5] obtained as directed in previous sections, should be diluted so as to contain not over 0.1 gram of manganese oxide equivalent per 100 ml. of solution. A cold saturated solution of ammonium sodium phosphate (microcosmic salt, 170 grams per liter; 9 ml. precipitates an equivalent of 0.1 gram of the oxide) is now added in slight excess. The solution is made strongly ammoniacal and heated to boiling, the boiling being continued until the precipitate becomes crystalline. After allowing to

[3] J. Pattinson, J. Chem. Soc., 35, 365, 1899.

[4] Gibbs, Chem. News, 17, 195, 1868.

[5] Some analysts prefer to add the phosphate reagent to the strongly ammoniacal solution, boiling hot.

(N.B. also F. A. Gooch and M. Austin, Am. J. Sci. (IV), 6, 233, 1898. A. A. Blair, "The Chemical Analysis of Iron," 8 ed., p. 106.)

settle until cold, the precipitate is filtered off (the filtrate being tested with more of the precipitating reagent to assure that an excess had been added), and dissolved in a little dilute hydrochloric or sulfuric acid.

Reprecipitation of the Phosphate.—The free acid is neutralized with ammonia added in slight excess until the odor is quite distinct, the solution heated to boiling, and a few ml. of additional phosphate reagent added. The crystalline precipitate is filtered into a weighed Gooch crucible, washed free of chlorides with very dilute ammonia ($AgNO_3+HNO_3$ test), dried and ignited to the pyrophosphate. The ignition is conducted, as in case of magnesium, by heating first over a low flame and gradually increasing the heat to the full power of the burner. The final residue will appear white or a pale pink.

$$Mn_2P_2O_7 \times 0.4997 = MnO,$$

$$Mn_2P_2O_7 \times 0.3870 = Mn.$$

NOTES.—Zinc, nickel, copper and other elements precipitated as phosphates should be absent from the solution. The separation from iron is generally made by the basic acetate method and manganese precipitated from the filtrate, free of other elements, as the peroxide MnO_2, by means of bromine added to the ammoniacal solution. Other oxidizing reagents may be used, as has been stated. The dioxide is dissolved in strong hydrochloric acid and the above precipitation effected.

VOLUMETRIC METHODS

VOLHARD'S METHOD FOR MANGANESE[6]

The method is based on the principle that when potassium permanganate is added to a neutral manganese salt all of the manganese is oxidized and precipitated. When this stage is reached any excess of permanganate is immediately evident by the color produced. The calculation of results may be based on the reaction,

$$3MnSO_4+2KMnO_4+2H_2O = 5MnO_2+K_2SO_4+2H_2SO_4,$$

or

$$5ZnSO_4+6MnSO_4+4KMnO_4+14H_2O = 4KHSO_4+7H_2SO_4+5ZnH_2\cdot 2MnO_3,$$

the ratio in either case being $2KMnO_4 = 3Mn$.

Procedure.—The material decomposed with hydrochloric and nitric acid and taken to fumes with sulfuric acid, as stated for the preparation of the sample, is cooled and boiled with 25 ml. of water until all salts have dissolved; then continue as follows: Transfer the mixture to a 500-ml. graduated flask and add an emulsion of zinc oxide in slight excess to precipitate the iron.

[6] Applicable for high grade ores.

Agitate the flask to facilitate the precipitation and see that a slight excess of zinc oxide remains when the reaction is complete. Now dilute the contents of the flask up to the mark with cold water, mix thoroughly and allow to stand a short time and partially settle. By means of a graduated pipette draw off 100 ml. of the clear supernatant liquid and transfer it to an 8-oz. flask. While the precipitate in the 500-ml. flask may appear large, it actually occupies but a very small space, and any error caused by it may consequently be neglected. Likewise the error in measurement due to change of temperature during the manipulation is insignificant. Heat the solution in the small flask to boiling, add two or three drops of nitric acid (which causes the subsequent precipitate to settle more quickly) and titrate with a standard solution of potassium permanganate. The permanganate causes a precipitate which clouds the liquid and it is therefore necessary to titrate cautiously and agitate the flask after each addition, and then allow the precipitate to settle sufficiently to observe whether or not the solution is colored pink. A little experience will enable one to judge by the volume of the precipitate formed, about how rapidly to run in the permanganate. The final pink tinge, indicating the end of the reaction, is best observed by holding the flask against a white background and observing the upper edges of the liquid. When this point is attained, bring the contents of the flask nearly to a boil once more and again observe if the pink tint still persists, adding more permanganate if necessary. In making this end-test avoid actually boiling the liquid, as a continual destruction of the color may sometimes thus be effected and the true end-point considerably passed. When the color thus remains permanent the operation is ended. Observe the number of ml. of permanganate solution used and calculate the result.

It is customary to use the same permanganate solution for both iron and manganese. Having determined the factor for iron, this may be multiplied by 0.2952 [7] to obtain the factor for manganese. It will be observed that $2KMnO_4$ are required for 3Mn, and in the reaction for iron that $2KMnO_4$ are required for 10Fe.

VOLUMETRIC DETERMINATION OF MANGANESE

BISMUTHATE METHOD

The determination of manganese by the bismuthate method is generally conceded to be the most accurate analytical procedure for determination of this element in iron and steel. It is simple and rapid, and generally can be accomplished without a previous separation being necessary. The principle

[7] An empirical factor 0.2984 is recommended by Cir. No. 26, National Bureau of Standards, in place of 0.2952 to obtain the manganese factor from iron.

of the process depends upon the fact that under certain conditions bivalent manganese can be quantitatively oxidized to permanganic acid by sodium bismuthate. This permanganic acid can now be titrated by a standard reducing agent such as sodium thiosulfate, arsenious acid, or ferrous sulfate.

The application of the bismuthate method to the determination of large amounts of manganese has been made by Thos. R. Cunningham and R. W. Coltman (J. Ind. and Eng. Chem., 16, 58, 1924). They recommend the following procedures:

FIG. 60.

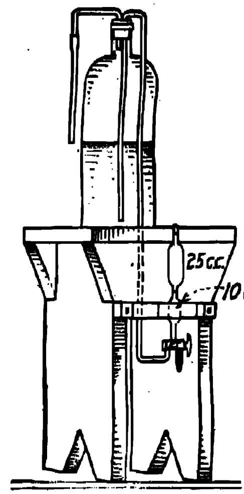


FIG. 61.

DETERMINATION OF MANGANESE IN MANGANESE ORES

Descriptions of the application of the bismuthate method to the determination of manganese in manganese ores, ferro-manganese, and manganese metal are given in the following paragraphs. The adaptation of the method to other products high in manganese is easily made after the operator becomes familiar with the conditions necessary.

Reagents Required.—(1) Concentrated nitric acid (specific gravity 1.42), freed from nitrous oxide by passing air through the solution for half an hour. If air from a compressor is used, it must be freed from oil and dust.

(2) Nitric acid of specific gravity 1.135, made by adding 500 ml. of the above acid to 1300 ml. of water.

(3) Dilute nitric for washing, prepared by adding 30 ml. of the concentrated acid described above to 1 liter of water.

(4) Sodium bismuthate. This reagent generally contains approximately 80% of $NaBiO_3$. If there is any doubt as to its oxidizing power, it may be tested as follows:

One-half gram is shaken up with 4 grams of potassium iodide and a little water in a stoppered flask. Fifteen milliliters of hydrochloric acid (specific gravity 1.19) are added and the solution is allowed to stand in the dark, with occasional shaking, until the bismuthate has entirely decomposed. The solution is diluted to 300 ml. and titrated with 0.1 N sodium thiosulfate, starch being used as indicator.

$$\text{One ml. of 0.1 N } Na_2S_2O_3 = 0.0140 \text{ gram } NaBiO_3.$$

(5) Ammonium persulfate (C.P.).
(6) Ferrous ammonium sulfate.
(7) Hydrogen peroxide (3%).
(8) Sulfurous acid. Solution of sulfur dioxide in water.
(9) Standardized 0.1 N potassium permanganate.

Solution of the Ore.—Grind the sample to pass 100-mesh and dry approximately 2.005 grams in a small 10-ml. weighing bottle, provided with a ground glass stopper, at 120° C. for one hour, or 105 to 110° C. for 2 hours. Cool the bottle and ore in a desiccator and weigh, the stopper being loosened for a second or so just before completion of the weighing. Empty the ore into a 400-ml. beaker, stopper the bottle and reweigh. Subtraction of the weight of the bottle, plus the residue, gives the weight of the dry ore transferred to the beaker. Dissolve the sample by heating with about 40 ml. of nitric acid (1 to 1) in a 400-ml. covered beaker, adding hydrogen peroxide in small portions until the violent evolution of oxygen is over and no black particles of ore remain. Rinse the cover glass and sides of the beaker with hot water and add bismuthate in small (0.05 gram) portions until a permanent precipitate of manganese dioxide forms. Any organic matter is thus destroyed and the excess of hydrogen peroxide removed. Boil for 2 or 3 minutes and then add sulfurous acid, drop by drop, until the solution clears. Boil the solution for 5 minutes longer and filter it into a 500-ml. volumetric flask. Wash the siliceous residue well with water and ignite it in platinum. Treat the residue with several drops of sulfuric acid (sp. gr. 1.84), several ml. of nitric acid (sp. gr. 1.42) and sufficient hydrofluoric acid (48%) to dissolve the silica and evaporate the solution to fumes of sulfur trioxide. Dissolve the residue in water and add to the solution in the flask. Bring the solution to a temperature of about 20° C., and make it up to the mark with water at this temperature.

Organic matter, including graphite, may best be destroyed by the addition of 30 to 35 ml. of perchloric acid (60%) to the 400-ml. beaker containing the HNO_3 solution of the sample and boiling until fumes of $HClO_4$ are freely evolved and MnO_2 begins to separate. Fifty (50) ml. of nitric acid (sp. gr. 1.135) are added, the solution boiled for several minutes to expel free chlorine, and the separated MnO_2 cleared by the addition of perhydrol (30% H_2O_2) drop by drop. The solution is boiled for about 3 minutes longer, filtered, etc., as described in the preceding paragraph.

With artificial manganese dioxide, where the weight of insoluble residue is insignificant, or in case the residue from an ore is flocculent and not sandy, the treatment with hydrofluoric and sulfuric acids may be omitted and the ore solution rinsed directly into the flask. Any barium in the ore will precipitate when the sulfuric acid solution of the residue is added to the main solution, but the barium sulfate does not interfere with the subsequent operations.

Trial Determination.—As it is desirable that the back titration with permanganate be not too great (say, from 10 to 20 ml.), it is best, when ores of unknown manganese content are being analyzed, to make a rough preliminary determination of the amount of manganese present, so that the amount of ferrous salt added may not be excessive. For this purpose transfer 25.0 ml. of the well-mixed solution with a pipette to a 300-ml. Erlenmeyer flask and add 12 ml. of nitric acid (specific gravity 1.42) and about 13 ml. of water. Cool this solution, add 1.7 grams of bismuthate, agitate the mixture for 1 minute, dilute with 50 ml. of water, and filter through asbestos, washing the residue with dilute (3%) nitric acid. Add 2.5 grams (weighed) of the solid, ferrous ammonium sulfate to the filtrate and titrate back with the 0.1 N permanganate. Calculate in the usual manner the weight of manganese present in the 25-ml. portion. As 100 ml. will be used in the actual determination, multiply the

result by 4, and calculate approximately the amount of bismuthate necessary (26 grams for 1 gram for manganese) and also a weight of ferrous sulfate that will give from 10 to 20 ml. in the back titration. The bismuthate is weighed out roughly, and the necessary ferrous sulfate weighed out to within half a milligram just preceding the titration.

Final Determination.—Transfer two 100-ml. aliquot portions with a pipette to 750-ml. Erlenmeyer flasks and add 50 ml. concentrated nitric acid and 50 ml. of water to each. (Total volume, 200 ml.) Cool the solutions (with ice, if possible) and add the calculated amount of bismuthate all at once. *Agitate the contents of the flask briskly for 1 minute*, add 200 ml. of cold water, and filter through asbestos, washing the residue with dilute nitric acid (solution No. 3) until the washings do not show the slightest trace of pink.

Place the weighed ferrous salt in a liter beaker and add the contents of the suction flask to it. Stir thoroughly until the permanganic acid has been decolorized and all the salt dissolved. Titrate at once with the standardized 0.1 N potassium permanganate to faint pink color.

Typical Analysis.—Two grams of ore were dissolved and made up to 500 ml.; two 100-ml. aliquot portions were oxidized and 9 grams of ferrous salt added to reduce the permanganic acid formed.

MANGANESE IN MANGANESE ORE

	Aliquot No. 1	Aliquot No. 2
Back titration, ml.	20.1	20.2
Equivalent of ferrous salt, ml.	228.6	228.6
Difference, ml.	208.5	208.4
Weight of manganese, gram	0.2291	0.2290
Percentage of manganese	57.26	57.24

ANALYSIS OF FERROMANGANESE AND MANGANESE METAL

The weight of sample used is governed by the manganese content; for 80% ferromanganese 0.30 gram may be used and for manganese metal, 0.25 gram. As there is no difficulty in obtaining a uniform sample, it is preferable to weigh out individual portions of the 100-mesh sample for the determination, instead of using an aliquot part of a large sample. The following procedure as regards the quantity of acid and final volume presupposes the presence of about 0.25 gram of manganese.

The sample is transferred to a 750-ml. Erlenmeyer flask and dissolved in 15 ml. of nitric acid (sp.gr. 1.135), 5 ml. of perchloric acid (60%) are introduced and the solution is boiled gently until the perchloric acid fumes strongly. The heat applied to the flask should be such that the perchloric acid refluxes down the sides, no great amount being lost by volatilization. After several minutes' heating, when a small amount of manganese dioxide has separated out, the liquid is cooled, treated with 10 ml. of water and 50 ml. of nitric acid (sp.gr. 1.135) and heated to boiling. Sulfurous acid or sodium nitrite solution in sufficient amount to just dissolve the manganese dioxide and to reduce any chromium present to the trivalent state is added and the solution is boiled for 5 minutes to expel oxides of nitrogen. After cooling to room temperature, sufficient nitric acid (sp.gr. 1.135) is added to bring the volume of the solution

to 250 ml., as shown by a mark on the flask, and the liquid is cooled to 10 to 15° C. The manganese is then oxidized with bismuthate and determined as described under "Analysis of Manganese Ore."

About 7.5 grams of sodium bismuthate are necessary for the oxidation and 9 grams of ferrous salt will reduce the permanganic acid resulting from a 0.2500-gram sample of 95% manganese metal.

The following data are from typical determinations on a sample of standard high-carbon ferromanganese:

MANGANESE IN FERROMANGANESE

Weight of sample g.	Ferrous salt g.	$KMnO_4$ Equivalent of ferrous salt ml.	Back titration ml.	0.1 N $KMnO_4$ consumed ml.	Per cent manganese
0.2500	7.5	191.3	13.4	177.9	78.15
0.2500	7.5	191.3	13.4	177.9	78.15
0.3000	9.0	229.2	15.7	213.5	78.19

MANGANESE IN MANGANESE METAL

No.	Weight of sample g.	Ferrous salt g.	$KMnO_4$ Equivalent of ferrous salt ml.	Back titration ml.	0.1 N $KMnO_4$ consumed ml.	Per cent manganese
1	0.2000	8.000	203.8	28.5	175.3	96.29
2	0.2500	9.000	229.2	10.0	219.2	96.32
3	0.2500	9.000	229.2	10.2	219.0	96.24

NOTES.—The conditions necessary for securing complete oxidation of large quantities of manganese and for preventing the permanganic acid from undergoing any appreciable decomposition during the subsequent filtration are summarized below.

Concentration of Nitric Acid.—The manganese should be present in a solution containing from 11% (specific gravity 1.062) to 22% (specific gravity 1.135) by weight of nitric acid. If the concentration of nitric acid falls much below 11%, the oxidation of the manganese will not be complete unless the time of shaking be increased to more than 1 minute.

Concentration of Manganese.—A solution of permanganic acid containing about 0.05 gram of manganese per 100 ml. has the maximum stability, but the weight of manganese can be increased to 0.1 gram in 100 ml. without danger of any material decomposition occurring during the time required for filtering off the excess of bismuthate. When the concentration of manganese rises much above 0.10 gram per 100 ml., the rate of decomposition of the permanganic acid is unduly rapid.

Amount of Sodium Bismuthate Necessary.—Approximately 26 grams of sodium bismuthate (79% $NaBiO_3$) must be used for 1 gram of manganese.

Time of Oxidation.—Shaking for 1 minute is sufficient to insure complete oxidation of the manganese to permanganic acid provided the foregoing conditions are adhered to.

Chlorides should be removed by taking the solution to fumes with H_2SO_4. The residue is dissolved in a small amount of water and the solution is evaporated to fumes a second time to insure the removal of every trace of chloride.

The only common metals that seriously interfere with the determination are cerium, cobalt, and sexivalent chromium. A method for the determination of cerium outlined by Metzger is exactly the same in principle as the bismuthate method for manganese. Any cerium present must therefore be separated as oxalate in acid solution, and the oxalic acid in the filtrate destroyed by evaporation with sulfuric and nitric acids as a preliminary to the determination of manganese.

The pink color produced by large amounts of cobalt interferes with the titration of permanganic acid. This can be overcome by separating the manganese from the bulk of the cobalt by precipitating it with sodium or potassium chlorate.

While trivalent chromium is in hot solution oxidized to the sexivalent state by bismuthate and by permanganic acid, the error caused by small amounts of trivalent chromium is not appreciable provided the solution is kept cold (10° C.), and is oxidized, filtered, and titrated as rapidly as possible. When more than a small percentage of chromium is present, it should be separated from the manganese by one of the several methods that have been proposed. Precipitation of the manganese from a nitric acid solution with sodium or potassium chlorate with subsequent filtration does not effect complete removal of chromium, but is useful in some cases. Fusion with sodium peroxide followed by filtration will give a complete separation, manganese remaining in the residue as oxide and chromium passing into the filtrate as sodium chromate. Watters precipitates chromium and ferric iron with zinc oxide and determines manganese in the filtrate, while Cain precipitates chromium and vanadium from a ferrous solution with cadmium carbonate and analyzes the filtrate for manganese. Sexivalent chromium interferes with the determination of manganese by the bismuthate method and must be reduced to the trivalent condition prior to the final oxidation with bismuthate.

Although any vanadium present is reduced by the ferrous sulfate added during the determination, it is re-oxidized by an equivalent amount of permanganic acid during the back titration, the manganese titration as a consequence being unaffected.

ANALYSIS FOR MANGANESE ORES [8]

Approximately 0.5000 gram of the agate ground sample is transferred to a small (10 ml.) weighing bottle provided with a ground glass stopper and heated for one hour or longer (to constant weight) at 120° C. (this temperature is recommended by the U. S. Bureau of Standards) in an oven through which there is passed a rapid stream of air that has been dried by passage through concentrated sulfuric acid and subsequently preheated to the temperature of the oven. The bottle and ore are allowed to cool in a desiccator and accurately weighed, the stopper being loosened for a second or so just before the completion of the weighing. The contents of the bottle are transferred to a 250-ml. beaker and the weighing bottle is stoppered and reweighed. Subtraction of the weight of the bottle plus any small amount of adhering ore from the original weight of the bottle plus the sample gives the exact weight of the dry ore transferred to the beaker. Manganese ores are frequently so hygroscopic as to render necessary the procedure described if the highest accuracy is desired. The use of 0.5000-gram sample is based on the assumption that the ore contains approximately 50% manganese. If the percentage of manganese should be higher or lower than 50% to the extent of 3% or more, a correspondingly smaller or larger weight should be taken in order that the weight of manganese will be approximately 0.2500 gram.

Fifty ml. of nitric acid (sp.gr. 1.135) and 1 to 3 ml. (a sufficient amount) of hydrogen peroxide (30%) diluted with 10 ml. of water are added to the beaker containing the sample. The solution is warmed and stirred until the mineral appears to have been decomposed completely and nothing but a comparatively white siliceous residue remains. The solution is then filtered on a 9-cm. paper into a 750-ml. Erlenmeyer flask and the paper and residue are washed thoroughly with nitric acid (sp.gr. 1.135) to remove all manganese nitrate. The residue is ignited in a 50-ml. platinum crucible at a low temperature, treated with 2 to 3 drops of sulfuric acid (sp.gr. 1.84) and 2 ml. of hydrofluoric acid

[8] Method of the Electro Metallurgical Company, supplied by T. R. Cunningham.

(48%) and the solution evaporated to dryness. The residue is fused with 1 or 2 grams (a sufficient amount) of potassium pyrosulfate, the melt dissolved in 25 ml. of nitric acid (sp.gr. 1.135) and added to the main solution.

Approximately one gram of sodium bismuthate is next added to the nitric acid solution of the manganese obtained as described in the preceding paragraph and, to insure the oxidation of hydrogen peroxide and of any organic matter, the liquid is boiled for several minutes. A sufficient volume of sulfurous acid to clear the solution is then introduced and the contents of the flask are boiled for five minutes to expel oxides of nitrogen, diluted with nitric acid (sp. gr.1.135) to a volume of 250 ml. (as shown by a mark on the flask), and cooled to a temperature of 10 to 15° C.

Provided the preceding instructions have been followed, the manganese will be present in a concentration of approximately 0.001 gram per ml. of solution The concentration of manganese (approx. 0.001 gram per ml.), the strength of nitric acid (sp.gr. 1.135), and the temperature (10 to 15° C.) specified are conditions which insure the maximum stability of the permanganic acid formed as further described. Approximately 7.0 grams of sodium bismuthate (80%) are added to the flask and the solution is briskly agitated for 1 minute, diluted with 250 ml. of cold water, and immediately filtered on a layer of acid washed asbestos supported on a 2″ alundum or perforated porcelain plate resting in a large glass funnel. To insure the complete oxidation of the manganese to permanganic acid under the conditions specified, it is essential that sodium bismuthate (80% $NaBiO_3$) be used in the ratio of at least 26 grams to every gram of manganese in solution. The filter and residue are washed with cold 3% nitric acid (made by diluting colorless nitric acid, sp.gr. 1.42, with cold water) until the washings are entirely colorless, when the filtrate and washings are immediately treated as described in the next paragraph. After having transferred the solution and excess of sodium bismuthate to the filter, at no time should the filter be allowed to suck dry until the washings are colorless, or else permanganic acid will be retained by the residue.

Nine grams of special C.P. ferrous ammonium sulfate taken from a well-mixed bottle of the salt are weighed on a clock-glass by means of an analytical balance and added to solution of permanganic acid. As soon as the reduction is complete and the salt has completely dissolved, the excess of $FeSO_4 \cdot (NH_4)_2SO_4$ is determined by titration with a 0.1 N solution of potassium permanganate.

Provided the operations are carried out as described, small amounts of chromium (2% or less) do not interfere with the determination. Larger amounts of chromium interfere to some extent and should be separated prior to the oxidation with bismuthate.

ANALYSIS OF SILICO MANGANESE ALLOYS[9]

Determination of Manganese.—Thirty-five one-hundredths (0.3500) of a gram of the 100-mesh sample of silico-manganese (65 to 70% manganese) or one (1.0000) gram of ferromanganese silicon is covered with from 5 to 10 ml. of hydrofluoric acid (48%) in a large platinum dish provided with a gold or platinum cover and when the reaction begins to slow up nitric acid (sp.gr. 1.42)

[9] Method of the Electro Metallurgical Company, submitted by T. R. Cunningham.

is added, a few drops at a time until the sample has dissolved completely. A further addition of about 5 ml. of hydrofluoric acid is made.

The contents of the dish are evaporated on a sand bath to approximately 2 ml., when 5 ml. perchloric acid (60%) are introduced and the solution evaporated to fumes of perchloric acid. The contents of the dish are transferred to a 750-ml. Erlenmeyer flask with 175 ml. of cold water and a few drops of sulfurous acid, and the solution is boiled for 4 or 5 minutes to expel free chlorine. Seventy-five (75) ml. of nitric acid (sp.gr. 1.42) free from nitrous fumes, and approximately 0.5 gram of sodium bismuthate are introduced and the liquid boiled for several minutes longer. Sulfurous acid is next added, dropwise, until the permanganic acid or any precipitate that formed has dissolved and an excess of about 1 ml. (sufficient to reduce to the trivalent form any chromium present in the solution) has been provided. The liquid is finally boiled for about 5 minutes to completely expel oxides of nitrogen, diluted with cold water to 250 ml. (as shown by a mark on the flask), cooled to 15° C. and treated as described in the third paragraph.

Providing the preceding instructions have been followed, the manganese will be present in a concentration of approximately 0.001 gram per ml. of solution. The concentration of manganese (approximately 0.001 gram per ml.), the strength of nitric acid (sp.gr. 1.135) and the temperature (10–15° C.) specified are conditions which insure the maximum stability of the permanganic acid as further described. Approximately 7 grams of sodium bismuthate (80%) are added to the flask and the solution is briskly agitated for 1 minute, diluted with 250 ml. of cold water and immediately filtered on a layer of acid-washed asbestos supported on a 2-in. alundum or perforated porcelain plate resting in a large glass funnel. To insure the complete oxidation of the manganese to permanganic acid under the conditions specified, it is essential that sodium bismuthate (80% $NaBiO_3$) be used in the ratio of at least 26 grams to every gram of manganese in solution. The filter and residue are washed with cold 3% nitric acid until the washings are entirely colorless, when the filtrate and washings are immediately treated as described in the next paragraph. At no time should the filter be allowed to suck dry until the washings are entirely colorless.

Nine (9.000) grams of ferrous ammonium sulfate, taken from a well-mixed bottle of the salt, are weighed on a clock-glass by means of an analytical balance and added to the solution of permanganic acid. As soon as the reduction is complete and the salt has completely dissolved, the excess of $FeSO_4 \cdot (NH_4)_2SO_4$ is determined by titration with an 0.1 N solution of potassium permanganate. The following equations show the reactions which occur:

$$H_2Mn_2O_8 + 10FeSO_4 + 7H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O.$$
$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

Provided the operations are carried out as described, small amounts of chromium (2% or less) do not interfere with the determination. Larger amounts of chromium interfere to some extent and should be separated prior to the oxidation with bismuthate.

Ferrous ammonium sulfate is used to reduce the permanganic acid formed. It is added in solid form, weighed to ±0.5 mg., just before the determination is started. This salt is preferable to ferrous sufate, as it goes into solution more readily. The manganese value of the ferrous salt must be known, and for this

purpose 5.0000 grams ($\pm$0.5 mg.) are titrated with the standard permanganate used. This titration should be made in sulfuric acid solution. If the salt is kept in a well-corked bottle, the standard will suffer practically no change, and having once been well mixed and standardized may be used indefinitely. If preferred, a 0.1 N solution of ferrous ammonium sulfate may be used instead of the solid salt.

The excess of ferrous salt is now titrated with a standardized solution of potassium permanganate, preferably of about 0.1 N strength. The permanganate may be standardized against National Bureau of Standards sodium oxalate, according to their recommendations, by means of pure manganous oxalate as hereinafter described, or against pure anhydrous manganous sulfate. Owing to the difficulty of preparing the latter salt so that it is of theoretical composition, the first two methods of standardization are preferable. After the normality of the solution against sodium oxalate has been determined, the theoretical factor—viz., 1 ml. 0.1 N $KMnO_4$ = 0.001099 gram of manganese—may be used.

Standardization against $MnSO_4$.—In order to determine the value of the permanganate in terms of manganese, manganous sulfate prepared in the following manner may be used:

Potassium permanganate (the ordinary C.P. product) was reduced in the presence of sulfuric acid with a little less than the calculated amount of oxalic acid, and the manganese dioxide formed is filtered off and discarded. The solution of manganese sulfate is treated with ammonium carbonate and the resulting manganese carbonate filtered and washed free from sulfates by decantation. This precipitate is added to a boiling solution of oxalic acid, and the manganous oxalate formed filtered and washed free from acid with distilled water. This product is converted to the sulfate by heating to constant weight at 480° to 520° C., with an excess of sulfuric acid. An accurately weighed amount of the pure manganous sulfate (2.7536 grams of $MnSO_4$, equivalent to 1.0018 grams of manganese) is dissolved and made up to 1 liter with nitric acid (specific gravity 1.135). One hundred and 200-ml. portions of this solution are oxidized with sodium bismuthate, filtered, and reduced by addition of accurately weighed amounts of ferrous ammonium sulfate, the excess of which is determined by means of 0.1 N permanganate that had been standardized against sodium oxalate. The relation between the ferrous ammonium sulfate and the permanganate is carefully determined. The results that are obtained, confirm Blum's statement that either manganous sulfate or sodium oxalate may be used as the primary standard for the bismuthate method, or expressed in another form, that the manganese is quantitatively oxidized to the heptavalent state.

$$2Mn^{++} + 5NaBiO_3 + 14H \rightarrow 2MnO_4^- + 5Bi^{+++} + 5Na^+ + 7H_2O.$$

The following substances interfere with the method; nitrous oxide, Cl, Ce, Co, Cr, V, P, Ag, Sb.

Iodometric Method for Determining Manganese.—Manganese is precipitated as dioxide according to the procedure described under the Gravimetric Methods—Bromate Method. The dioxide placed in the flask in which the precipitation is made is treated with 50–75 ml. of water and 5 ml. of 20% solution of $KF \cdot 2H_2O$ and 5 ml. 4 N H_2SO_4 and about 1–2 grams of KI. The liberated iodine is titrated with 0.1 N $Na_2S_2O_3$ solution. Use a weaker solution of

$Na_2S_2O_3$ if the amounts of Mn are small. Near the end-point the flask should be shaken and the titration completed.

Empirical factors—Zinc present and iron absent: 1 ml. 0.1 N $Na_2S_2O_3$, $0.002747 \times 1.02 = 0.002801$ g. Mn. Iron present: 1 ml. 0.1 N $Na_2S_2O_3$, $0.002747 \times 1.01 = 0.002774$ g. Mn.

Ferrous Sulfate Method for Manganese.—Separate manganese as dioxide according to the method described under Gravimetric Methods—Bromate Method. To the washed precipitate add dilute sulfuric acid and an excess of standard ferrous sulfate. Titrate the excess with standard potassium permanganate. Convert the two solutions to equivalent volumes and multiply the difference ($FeSO_4$–$KMnO_4$) by the empirical factors given above under Iodometric Method.

NOTES.—Kolthoff and Sandell[10] state that chromium does not affect results. Molybdates, except in small amounts, give results that are too low; tungsten to a less extent gives low results. Phosphoric acid in appreciable quantities interferes. Cobalt and iron may be present to the extent of 70 mg. with 75 mg. Mn. Small amounts of lead, nickel and bismuth may be present. Chlorides are oxidized by the bromate and do not interfere. Ammonium salts should not be present in quantity. Vanadium is absorbed by the MnO_2, but does not interfere with the Ferrous Sulfate Method.

FORD-WILLIAMS METHOD FOR MANGANESE

In this method manganese dioxide is precipitated by potassium chlorate from a nitric acid solution. Chlorine dioxide gas that is formed by the reaction is boiled off, the manganese dioxide is dissolved by an excess of ferrous sulfate or oxalic acid and the excess of the reducing agent is titrated with standard potassium permanganate.

Reagents.—0.03 N solutions of potassium permanganate, ferrous sulfate (or oxalic acid or sodium oxalate). See Manganese in Steel for preparation of reagents, chapter on Iron.

Procedure.—A sample of about 3 grams of steel is dissolved in 60 ml. of dilute nitric acid (sp.gr. 1.2). (For ores see Preparation and Solution of the Sample.) The solution is evaporated to about 50 ml. and 50 ml. concentrated nitric acid added and about 3 grams of potassium chlorate. The solution is boiled for about 15 minutes and the flask removed from the source of heat. ($KClO_3$ added to boiling HNO_3 will cause an explosion.) Fifty ml. more of nitric acid (d. 1.42) are added and 3 grams of $KClO_3$ and the solution again boiled. After cooling under water of a tap, the precipitated MnO_2 is filtered onto asbestos (an asbestos mat over a plug of glass wool in a funnel), and is washed with concentrated nitric acid until free from iron and then with water until free from acid.

The precipitate is now placed in a flask, together with the asbestos, 50 ml. of the standard ferrous sulfate are added and the solution diluted to about 200 ml. The mixture is shaken to dissolve the MnO_2 and the excess of 0.03 N ferrous solution is titrated with 0.03 N potassium permanganate.

Calculation.—If the permanganate is standardized against sodium oxalate, the oxalate equivalent of 1 ml. of the permanganate solution multiplied by 0.4099 will give the equivalent manganese per ml., according to theory (see note).

[10] Ind. Eng. Chem., Anal. Ed. 1, 181 (1929).

NOTE.—The nitric acid must be free from nitrous acid as this reduces MnO_2.
The permanganate equivalent is 5/3 of the permanganate equivalent of the Volhard's method, in which the valence of manganese is reduced from 7 to 4 Here the valence is reduced to 2. It is advisable to get the value of the reagents in terms of manganese on standard samples of manganese.

AMMONIUM PERSULFATE METHOD FOR DETERMINING SMALL AMOUNTS OF MANGANESE BY COLORIMETRIC COMPARISON OR BY TITRATION [11]

The process depends upon the oxidation of manganous salts to permanganate by ammonium persulfate in presence of a catalytic agent such as silver nitrate:

$$2Mn(NO_3)_2+5(NH_4)_2S_2O_8+8H_2O=5(NH_4)_2SO_4+5H_2SO_4+4HNO_3+2HMnO_4.$$

The reaction takes place equally well in sulfuric or in nitric acid solution, or in a mixture of the two. The essential point is the presence of a sufficient amount of silver nitrate catalyst (fifteen times Mn present).

Procedure.—One gram of ore is dissolved in hydrochloric acid, followed by sulfuric and taken to fumes as directed under Preparation and Solution of the Sample. The sulfate taken up with water is made to a volume of 100 ml. If the color comparison is to be made the solution should be filtered through a dry filter, otherwise the filtration may be omitted. Twenty ml. (equal to 0.2 gram) of the material is taken for the test. In the case of steel, 0.1 to 0.2 gram of the drilling, dissolved in dilute nitric acid, is taken.

Oxidation.—The solution is transferred to a test-tube, 1×10 in., if the color comparison is to be made, or into a 150-ml. Erlenmeyer flask, if the sample is to be titrated. Fifteen ml. of silver nitrate solution (1.5 grams $AgNO_3$ per liter of water), are added; the solution heated to 80 to 90° C. by placing the receptacle in hot water, and then 1 gram of ammonium persulfate added. When the color commences to develop the sample is cooled in cold water, while the evolution of oxygen continues. The sample is poured into the comparison tube and the color compared with that obtained from an ore or steel sample of known manganese content, run in the same way.

In the titration method the solution in the Erlenmeyer flask is diluted to about 100 ml., 10 ml. of 0.2% salt solution added, and the sample titrated with standard sodium arsenite until the permanganate color is destroyed. The ml. of the reagent used multiplied by the factor per ml. in terms of manganese equals weight of manganese in the sample titrated.

NOTE.—Arsenious acid reagent is made by dissolving 10 grams of arsenious oxide in water containing 30 grams of sodium carbonate. The solution is diluted to 1 liter. 125 ml. of this solution are diluted to 2000 ml. This latter reagent is standardized against an ore or sample of steel of known manganese content, following the directions given under the procedure outlined. NaCl is added to precipitate the excess of silver, which is removed to prevent oxidation during titration.

[11] W, V, Cr interfere, but may be removed by precipitation with ZnO emulsion.

OXIDATION WITH KIO_4[12]

Manganous ion is oxidized to $HMnO_4$ in nitric acid solution by a slight excess of KIO_4. The reaction is

$$2Mn(NO_3)_2+5KIO_4+3H_2O=2HMnO_4+5KIO_3+4HNO_3$$

The color is stable for a long period of time.

General Procedure.—The substance to be examined is brought into a solution containing per 100 ml. at least 10–15 ml. of conc. H_2SO_4, and 20 ml. of conc. HNO_3 or 5–10 ml. of conc. H_3PO_4. Reducing substances should be removed by previous oxidation with HNO_3 or by adding a little persulfate if carbon compounds are present as in steels. Chloride must be removed by evaporation to fumes of SO_3. Then 0.2 to 0.4 g. of KIO_4 or $NaIO_4$ or an equivalent amount of $Na_3H_2IO_6$ is added and the solution is boiled for a minute, kept hot for 5–10 min., cooled, diluted to a proper volume and compared with a solution of known Mn content, prepared in a similar manner. Not more than 1 mg. of Mn per 50 ml. should be present at the time of comparison.

If iron is present, either sulfuric or phosphoric acid must be present. Ferric periodate is insoluble in fairly concentrated nitric acid but dissolves in the other acids.

Ammonium salts do not interfere nor do the metallic ions that are commonly present unless they are colored.

The method is applicable to the determination of Mn in water, soil, ores and other materials in which the element is present in small amounts.

MANGANESE IN STEEL

From 0.5 to 1 g. of the steel is dissolved in nitric acid and the carbon is destroyed by ammonium persulfate. Make the solution up to 100 ml. after adjusting the acid concentration to 20 ml. of conc. HNO_3 and 5–10 of conc. H_3PO_4. Add 0.5 g. of KIO_4 and follow the general procedure for the heating and color comparison.

OXIDATION OF MANGANESE TO PERMANGANATE BY RED LEAD

Red lead oxidizes manganese in nitric acid solution to permanganate. The method is suitable for determining this element in steel and iron in presence of molybdenum, aluminum, tungsten, copper and nickel, in amounts such as are apt to be present. The method is given in the chapter on Iron in the Analysis of Iron and Steel.

[12] Willard and Greathouse, J. Am. Chem. Soc., 39, 2366 (1917).

MERCURY[1]

Hg, *at.wt.* 200.61; *sp.gr.* 13.595; *m.p.* −38.9°; *b.p.* 357.33° C.; *oxides*, Hg_2O, HgO

The element is not abundant, nor widely distributed. The metal is found in the upper portions of cinnabar deposits, a mineral HgS, the chief source of the element. The element has been found in quartz, sandstone, schists, iron pyrites, bituminous substances, eruptive and sedimentary rocks of all ages. It occurs as chloride in horn silver. It is occasionally associated with zinc ores. It is generally found locally concentrated. The minerals that are more common are: cinnabar, HgS; calomel, Hg_2Cl_2; coloradoite, HgTe; amalgam, Ag·Hg; livingstonite, $HgSb_4O_7$; tiemannite, HgSe.

DETECTION

Metallic mercury is recognized by its physical properties. It is the only metal which is a liquid at ordinary temperatures. The element forms a convex surface when placed on glass.

Mercury in the mercurous form is precipitated by hydrochloric acid as white mercurous chloride, HgCl. This compound is changed by ammonium hydroxide to the black precipitate of metallic mercury and nitrogen dihydrogen mercuric chloride.

Mercury in the mercuric form is not precipitated by hydrochloric acid. The sulfide of the element is thrown out from an acid solution as black HgS. The precipitate first appears white, changing to orange-yellow, then brown and finally to black, as the H_2S gas is passed into the solution. The element is distinguished from the other members of the group by the insolubility of its sulfide in yellow ammonium sulfide and in dilute nitric acid.

[1] We have evidence that the knowledge of metallic mercury dates back to 1600 B.C. Aristotle refers to mercury as "fluid silver." Mercury was used by the ancients in gilding, the sulfide was employed as a pigment. Today mercury finds use in thermometers and barometers. It is employed in vacuum pumps and as a confining liquid for gases. It is used in mercury vapor lamps. It forms amalgams with metals; silver and tin amalgams are employed in filling teeth, sodium amalgam is used as a reducing agent. The element is extensively used in the extraction of gold from its ores by formation of gold amalgam. Mercury salts which are at all soluble are poisonous, as well as the vapor of mercury. Compounds of mercury are used for skin diseases, as eczema, and for increasing secretions of internal body fluids.

If the mercury sulfide is dissolved in aqua regia, the nitric acid expelled by taking to dryness, then adding hydrochloric acid and evaporating again to dryness, the residue taken up with a little hydrochloric acid, diluted with water, and treated with a solution of stannous chloride, a white precipitate of mercurous chloride is first formed, which is further reduced to metallic mercury by an excess of the reagent.

ESTIMATION

In preparation of the sample for analysis the volatility of mercury and its compounds, especially the chloride, the iodide, and sulfide, must be borne in mind. This volatilization takes place even in boiling solutions, unless provision is made for carrying out the decomposition in flasks with condensers. Fusions with appropriate fluxes are made in combustion tubes with provision to absorb the evolved gases.

Mercury amalgams are best decomposed by nitric acid. The oxides are soluble in acids, the mercurous oxide forming the difficultly soluble mercurous chloride with HCl.

Decomposition of the sulfide of mercury is accomplished by treating in a flask, carrying a short-stemmed funnel, with sulfuric acid and potassium permanganate, according to Low's Method given under " Volumetric Thiocyanate Method later in this chapter. Mercuric Sulfide is readily soluble in constant-boiling HI.

Decomposition of ores may be effected in a combustion tube, drawn out at one end and bent at right angles, so as to dip into water. Hillebrand and Lundell recommend mixing the material with copper oxide and anhydrous quicklime and inserting well into the tube. Ignited calcium oxide, asbestos plug and copper plug are placed on either side of the charge, in the order named, this completes the packing of the tube. Carbon dioxide is conducted into the straight end of the tube, the tube is heated and the mercury swept into water and dilute nitric acid, in flasks connected in series. Mercury is converted to nitrate and determined according to the Thiocyanate Method—page 580.

Direct decomposition is accomplished in a specially constructed apparatus, a description of which is given under Gravimetric Methods.

The volatility of mercury compounds, especially the chloride, makes it necessary to use great care in decomposing substances in which it is contained. Fusion of compounds with sodium carbonate will completely volatilize mercury. Volatilization also takes place in evaporations by boiling solutions containing the mercury compounds. The loss that occurs is dependent on the form of apparatus. In flasks this is the least volatile (approximately 5%) while in

open dishes this may reach nearly 50% of the mercury originally present.[2] Decompositions, therefore, cannot be carried out in open vessels, and must be conducted in combustion tubes, with special precautions for absorbing the volatilized mercury, or in flasks with provision for condensing the evolved mercury compounds. The matter is dealt with later.

SEPARATIONS

Direct Volatilization.—See under Gravimetric Methods.

Separation of Mercury from the Iron and Zinc Groups, or from the Alkaline Earths and the Alkalies.—Mercury is precipitated as a sulfide from an acid solution of the mercuric salt by hydrogen sulfide, together with the members of the hydrogen sulfide group. Sufficient acid should be present to prevent the precipitation of zinc sulfide. Iron, aluminum, chromium, manganese, cobalt, nickel, zinc, the alkaline earths and the alkalies remain in solution.

Separation of Mercury from Arsenic, Antimony, and Tin.—The sulfides obtained by passing hydrogen sulfide into an acid solution, preferably of the chlorides, are digested with yellow ammonium sulfide solution. Arsenic, antimony and tin dissolve, whereas mercury sulfide remains insoluble. Sulfides of the fixed alkalies dissolve mercury as well as arsenic, antimony and tin, so cannot be used in effecting a separation.

Separation from Lead, Bismuth, Copper and Cadmium.—These elements remain with mercury upon removal of arsenic, antimony and tin as their sulfides are insoluble in ammonium sulfide. (CuS slightly soluble.) The precipitated sulfides are transferred to a porcelain dish and boiled with dilute nitric acid, sp.gr. 1.2 to 1.3. After diluting slightly with water the solution is filtered and the residue of mercuric sulfide washed with dilute nitric acid and finally with water. If much lead is present in the solution it is apt to contaminate the residue by a portion being oxidized to lead sulfate and remaining insoluble. In this case the residue is treated with aqua regia, the solution diluted and mercury chloride filtered from $PbSO_4$ and free sulfur. Mercury is best determined as HgS by the Ammonium Sulfide Method described later. Traces of lead do not interfere, as lead is completely removed by remaining insoluble in potassium hydroxide, whereas mercury sulfide dissolves. See method.

Separation from Selenium and Tellurium.—The mercury selenide or telluride is dissolved in aqua regia, chlorine water added and the solution diluted to 600 to 800 ml., phosphorous acid is added and the solution allowed to stand for some time; mercurous chloride is precipitated, selenium and tellurium remaining in solution. Selenium and tellurium will precipitate in hot concentrated solutions when treated with phosphorous acid, but not in dilute hydrochloric acid solutions.

Mercury in Organic Substances.—The material is decomposed by heating in a closed tube with concentrated nitric acid, or by heating in a flask with filter funnel short-stemmed, with 10% H_2SO_4 and sufficient $(NH_4)_2S_2O_8$, added in small portions until the organic matter is decomposed.

[2] Hillebrand and Lundell—"Applied Inorganic Analysis," John Wiley and Sons.

GRAVIMETRIC METHODS

DETERMINATION OF MERCURY BY PRECIPITATION WITH AMMONIUM SULFIDE

The following method, suggested by Volhard, is generally applicable for determination of mercury. The element is precipitated by ammonium sulfide as HgS. The precipitate dissolved in caustic is again thrown out by addition of ammonium nitrate to the thio salt solution of mercury.

$$Hg(SNa)_2+2NH_4NO_3=2NaNO_3+(NH_4)_2S+HgS.$$

Procedure.—The acid solution of the mercuric salt is nearly neutralized by sodium carbonate, and is then heated with a slight excess of ammonium sulfide reagent, freshly prepared. Sodium hydroxide solution is added until the dark-colored liquid begins to lighten. The solution is now heated to boiling and more sodium hydroxide added until the liquid is clear. If lead is present it will remain undissolved and should be filtered off. Ammonium nitrate is now added to the solution in excess and the mixture boiled until the greater part of the ammonia has been expelled. The clear liquid is decanted from the precipitate through a weighed Gooch crucible and the precipitate washed by decantation with hot water and finally transferred to the crucible and washed two or three times more. The mercuric sulfide is dried at 110° C. and weighed as HgS.

$$HgS\times 0.8622=Hg \quad \text{or} \quad \times 0.9310=HgO.$$

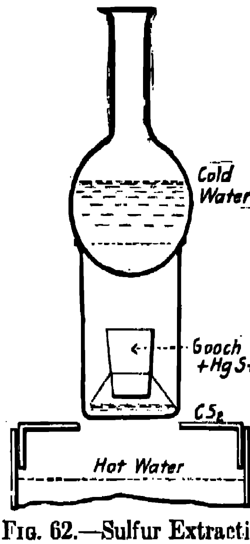


FIG. 62.—Sulfur Extraction Apparatus.

NOTES.—Alumina and silica are apt to be present in caustic.

Free sulfur may be removed, if present, by boiling with sodium sulfite, $Na_2SO_3+S=Na_2S_2O_3$. The sulfur may be extracted with carbon disulfide. The Gooch crucible is placed upon a glass tripod in a beaker, containing carbon disulfide and a round-bottomed flask filled with cold water is placed over the mouth of the beaker to serve as a condenser, Fig. 62. By gently heating over a water bath for an hour the sulfur is completely extracted from the sulfide. Carbon disulfide is removed from the precipitate by washing once with alcohol followed by ether. The residue is now dried and weighed.

If the mercuric sulfide is collected on a glass or porcelain filter crucible, the sulfur present may be determined after weighing the impure HgS—S misture by adding cold constant-boiling HI, stirring, washing with four 5 ml. portions of 5–10% HI, then with cold water, drying for 2 hours in a vacuum disiccator and weighing.[3]

Mercury in form of mercuric chloride may be reduced to the difficultly soluble (HgCl) mercurous chloride, by means of a solution of phosphorous acid, and weighed as such, after washing and drying at 100°–105° C. Results are generally low.

[3] Caley and Burford, Ind. Eng. Chem., Anal. Ed. 8, 43 (1936).

DETERMINATION OF MERCURY AS THE METAL BY THE AMALGAMATION METHOD

This excellent direct method for determining mercury in ores depends upon the distillation of the metal from the dry material, reducing the material, if necessary, by means of iron filings or lime, and collecting the metal on a weighed sheet of gold or silver. For purpose of effecting a reduction of the mercury Eschka [4] suggested the use of iron; Erdmann and Marchand recommended lime; in ores containing arsenic zinc oxide is recommended. By the method 50 mg. may readily be determined, and as much as 100 mg. if gold is used to collect the volatilized mercury. If iron filings are used these should be fairly fine and free of dust. Grease should be removed by treating the filings with alcohol, followed by ether and then drying thoroughly.

Apparatus.—A thin-spun iron or nickel crucible with a rim to which the sheet of gold or silver will fit snugly is recommended. The crucible is inserted in a circular opening in an asbestos board, just large enough for the crucible to fit snugly and protrude about half its height above the board. This prevents

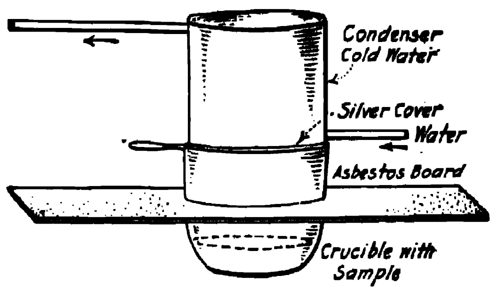


FIG. 63.—Apparatus for Determining Mercury.

the flame from heating the upper portion. The disc of gold or silver is cooled by contact with a cylindrical condenser, through which cold water circulates. An Erlenmeyer flask may be used as is shown in Fig. 47 (chapter on Fluorine) The Whitton apparatus is shown in Fig. 63.

The Whitton apparatus possesses novel features which render the assay more accurate and reliable, the manipulation simpler and the time rapid. It consists of a steel retort with a cover of sheet silver, and above these a flat-bottomed cooling dish of brass; all clamped tightly together. Thus the distillation is performed in a closed retort, which prevents the escape of mercury vapor, and renders careful regulation of the heat unnecessary.

An important advantage lies in the use of the steel retort. It should be recognized that mercury vapors will condense upon any surface below the boiling point of mercury, 357.82° C., whether that surface be ore with which they will amalgamate or not. The steel retort is a good conductor of heat, and thus all portions of it are readily brought above this temperature, while the foil is kept below this temperature by its contact with the bottom of the cooling dish; thus the vapor must condense upon the foil and not upon any other portions of the exposed inner surface of the retort. The silver foil used in the

[4] A. Eschka, Dinglers Polytech. J., 204, 47, 1872. G. T. Holloway, Analyst, 31, 66, 1906.

apparatus can easily be replaced at a very small expense. One piece of foil will last for from five to ten assays.

The time required for an assay is about thirty minutes. By using two sets of apparatus and four foils, weighing up the first pair of foils while the second pair is in use, it may be made in fifteen minutes.

Procedure.—The sample is weighed and placed in the crucible " *a* " of the apparatus. Not over 0.1 g. of mercury should be present in the amount of material taken. Five to 10 grams of iron filings are intimately mixed with the product in the crucible and additional filings sprinkled over the surface. Sulfide ores should be mixed with about twice their weight of a flux of a zinc oxide and sodium carbonate in the proportion of 4 : 1, and about five times the weight of iron filings added, mixing well. The silver foil is weighed and placed between the crucible and cooler at " *b*."

The bottom of the crucible is gradually heated with a small flame of a Meker or burner of similar type, being careful to not overheat. The top of the crucible should remain cold, otherwise mercury will be lost. After heating for thirty minutes, the apparatus is allowed to cool without disconnecting the condenser. The foil is now removed, dipped in alcohol and dried in a desiccator over fused calcium chloride. The increase in weight of the foil is due to metallic mercury.

NOTE.—It is advisable to repeat the test with a clean foil to be sure that all mercury, has been obtained from the sample. The mercury may be removed from the foil by heat.

Gold is preferable to silver for on its surface minute amounts of mercury are visible and gold absorbs a larger amount on its surface than will silver. The silver foil, however, is very satisfactory.

Determination of Mercury in Cyanide Solutions.—The procedure recommended by W. J. Sharwood with use of the apparatus described above is given in the latter portion of this chapter.

DETERMINATION OF MERCURY BY ELECTROLYSIS

Mercury is readily deposited as a metal from slightly acid solutions of its salts.

Procedure.—The neutral or slightly acid solution of mercuric or mercurous salt is diluted in a beaker to 150 ml. with water and 2 to 3 ml. of nitric acid added. The solution is electrolyzed with a current of 0.5 to 0.1 ampere, and an E.M.F. of 3.5 to 5 volts. A gauze cathode is recommended, or a platinum dish with dulled inner surface may be used. One gram of mercury may be deposited in about fifteen hours (or overnight). The time may be shortened to about three hours by increasing the current to 0.6 to 1 ampere.

The metal is washed with water without interrupting the current and then with alcohol. After removing the adhering alcohol with a filter paper, the cathode is placed in a desiccator containing fused potash and a small dish of mercury. The object of this mercury is to prevent loss of the deposit by vaporization.

The increased weight of the cathode is due to metallic mercury.

NOTES.—In the electrolysis of mercuric chloride turbidity may be caused by formation of mercurous chloride by reduction, but this does no harm, as the reduction to metallic mercury follows.

Mercury may be electrolyzed from its thio-salt solutions, obtained by dissolving its sulfide in concentrated sodium sulfide.

VOLUMETRIC DETERMINATION OF MERCURY

SEAMON'S VOLUMETRIC METHOD[5]

Seamon's Volumetric Method.—Weigh 0.5 gram of the finely ground ore into an Erlenmeyer flask of 125 ml. capacity. Add 5 ml. of hydrochloric acid (1.19) and allow it to act for about ten minutes at a temperature of about 40° C., then add 3 ml. of nitric acid (1.4) and allow the action to continue for about ten minutes longer. The mercury should now all be in solution. Now if lead be present, add 5 ml. of concentrated sulfuric acid; it may be omitted otherwise. Dilute with 15 ml. of water and then add ammonia cautiously until the liquid is slightly alkaline. Bismuth, if present, will be precipitated. Acidify faintly with nitric acid, filter, receiving the filtrate in a beaker, and wash thoroughly.

Add to the filtrate 1 ml. of nitric acid (1.4) that has been made brownish in color by exposure to the light, and titrate with a standard solution of potassium iodide until a drop of the liquid brought into contact with a drop of starch liquor, on a spot-plate, shows a faint bluish tinge. It is a good plan to set aside about one-third of the mercury solution and add it in portions until the end-point is successively passed, finally rinsing in the last portion and titrating to the end-point very carefully.

Deduct 0.5 ml. from the burette reading and multiply the remaining ml. used by the percentage value of 1 ml. in mercury to obtain the percentage in the ore.

The standard potassium iodide solution should contain 8.3 grams of the salt per liter. Standardize against pure mercuric chloride. Dissolve a weighed amount of the salt in water, add 2 ml. of the discolored nitric acid and titrate as above. One ml. of standard solution will be found equivalent to about 0.005 gram of mercury, or about 1% on the basis of 0.5 gram of ore taken for assay.

The precipitate of red mercuric iodide which forms during the titration may not appear if the amount of mercury present is very small, but this failure to precipitate does not appear to affect the result.

Iron, copper, bismuth, antimony, and arsenic, when added separately to the ore, did not influence the results in Seamon's tests. Silver interferes. Duplicate results should check within 0.1 to 0.2 of 1%.

VOLUMETRIC THIOCYANATE METHOD FOR MERCURY[6]

A sample containing 0.1 to 0.5 g. Hg placed in a flask is decomposed by adding 10 ml. dilute H_2SO_4 (1 : 1) and about 0.5 g. $KMnO_4$ crystals. The mixture is agitated and heated to fumes. The solution cooled is diluted to

[5] "Manual for Assayers and Chemists," p. 112.
[6] A. H. Low, Chemist-Analyst, 29, 13 (1919).

50 ml. with cold water, then boiled and the MnO_2 dissolved by adding a few crystals of oxalic acid (small portions at a time).

The solution is filtered, and any residue washed with dilute (1 : 10) H_2SO_4. The sulfide group is now precipitated with H_2S and filtered off. The precipitate, transferred to a flask, with short-stemmed funnel, is digested for some time with dilute HNO_3 (2 : 1), the solution then diluted with hot water and filtered and the HgS washed with dilute HNO_3 (1 : 1).

The HgS is transferred to a flask with a few ml. of hot water and then 5 ml. of strong H_2SO_4 and 0.5 g. $KMnO_4$ are added and the mixture heated to fumes. Oxalic acid crystals are added until the MnO_2 dissolves and the mixture again heated to fumes to destroy the excess of oxalic acid. The solution, cooled, is diluted to 100 ml. (It should now be clear.)

About 5 ml. of a saturated solution of ferric ammonium sulfate solution (acidified with HNO_3) are added and the solution titrated with 0.1 N thiocyanate solution.

One ml. 0.1 N thiocyanate = 0.01003 g. Hg.

Solutions. Ferric Indicator.—Make a saturated solution of ferric ammonium sulfate or ferric sulfate. Add sufficient nitric acid (freed from nitrous acid by heating) to clear the solution and produce a pale yellow color. Five ml. of this solution (the Editor prefers less) is used in the test. Ferric nitrate may be used if the sulfate is not available.

Thiocyanate Reagent.—A tenth normal solution may be made by dissolving 7.4 grams of NH_4CNS or 9.2 grams of KCNS in water and diluting to a liter. The solution may be standardized against a standard silver solution, containing 0.01079 grams silver per ml.

Forty ml. of the silver solution is measured into a beaker or Erlenmeyer flask and diluted to about 100 ml. The ferric indicator is added and the solution is titrated with the thiocyanate solution. Each addition of the thiocyanate will produce a temporary red color, which fades out as long as there is silver uncombined with thiocyanate. A drop in excess of the thiocyanate produces a permanent faint red color.

The thiosulfate may be standardized against pure mercury dissolved in dilute HNO_3 following the procedure given above.

Mercury in Organic Matter.—The compound is decomposed by the method of Carius by heating in a closed tube (see page 265) with conc. nitric acid (d. 1.42). The amount of nitric acid used should not exceed 3 ml. per 50 ml. tube, otherwise an explosion may result.[7] The acid solution is neutralized by addition of sodium hydroxide and sufficient excess of the alkali added to insure a slight excess. Pure potassium cyanide is now added in quantity sufficient to dissolve the mercuric oxide precipitate, and the solution saturated with H_2S gas. Ammonium acetate is added and the solution boiled until nearly all the NH_3 has been expelled. The precipitate is allowed to settle and then filtered off and washed with hot water, and then with hot dilute HCl and again with water. The precipitate is dried at 110° C. and weighed as mercuric sulfide, HgS.

Note.—Should free sulfur be present its removal is accomplished by extraction with pure CS_2, see page 577.

[7] Fresenius, Quant. Chem. Anal., 2, 118, 1915.

Other Volumetric Methods.—Mercurous ion may be oxidized by potassium permanganate or by ceric sulfate in excess.[8] Potassium iodate may be used for the direct oxidation of calomel under iodine monochloride conditions (see chapter on Standard Solutions). Mercury may be precipitated as zinc mercuric thiocyanate and the thiocyanate titrated with standard iodate solution. Mercurous mercury may be titrated with standard chloride or bromide solution using bromphenol blue as adsorption indicator.[9] Mercuric chloride may be titrated with standard potassium iodide to the appearance of a permanent red turbidity. Mercuric ion may be precipitated as mercuric pyridine bichromate and weighed, or the bichromate may be titrated by conventional methods.[10]

DETERMINATION OF MERCURY IN ZINC AMALGAM

The method is applicable to the determination of mercury in "battery zincs" in which mercury is present to the extent of 1–3%. The procedure has been used by the N. Y., N. H. and H. Railroad.

Procedure.—Accurately weigh about 5 grams of the finely divided alloy, place in a beaker and dissolve in about 75 ml. of dilute HCl (1 : 1) and heat gently for about three hours. The zinc goes into solution, whereas the mercury and lead remain undissolved as metals. Decant off the solution and wash the metals several times with hot distilled water by decantation. Transfer to a weighed porcelain crucible, carefully decanting off the water. Expel the remaining water by drying in an oven at 100° C. Cool in a desiccator and weigh. Now gently ignite at a dull red heat. Cool in a desiccator and again weigh. The loss of weight is due to the volatilization of mercury.

Note.—Conduct the ignition under a hood for 3–5 minutes.

DETERMINATION OF MERCURY IN AMALGAMATED ZINC[11]

Procedure.—Remove the rolling compound from the surface with appropriate solvents and cut the dry zinc into small pieces. Weigh about 20 grams into a 300-ml. beaker. Dissolve the metal with HCl (1 : 1), facilitating the solution process by decanting the spent acid through a hard filter before a fresh portion is added.

When no more H is evolved compress the residue in the bottom of the beaker with a flattened glass rod and drain off the liquid through the filter. Wash with hot water by decantation until acid free. Dry the filter at 100° C. and brush from it the small amount to the main residue in the beaker. There is little danger of mercury loss to this point in the procedure provided there be sufficient lead present to absorb the mercury, but great care must be taken when this amalgam is dissolved.

[8] The latter method is very satisfactory. Willard and Young, J. Am. Chem. Soc., **52**, 557 (1930).

[9] Zombory, Z. anal. Chem., **184**, 237 (1929); Zombory and Pollak, ibid., **215**, 255 (1933); Kolthoff and Larson, J. Am. Chem. Soc., **56**, 1881 (1934).

[10] Spacu and Dick, Z. anal. Chem., **76**, 273 (1929); Furman and State, Ind. Eng. Chem., Anal. Ed. **8**, 467 (1936).

[11] Alfred Kundert, Research and Development Department, French Battery Co., Madison, Wisconsin. From the Chemist-Analyst.

Cover the beaker with a watch glass and dissolve the residue without heat in 2 or 3 ml. HNO_3 (1 : 1). Add a slight excess of Br water and rotate until dissolved, then add 25 ml. H_2O. Ignore any white undissolved salt but be certain that Hg is all converted. (Add dropwise a concentrated solution Na_2CO_3 until a slight flocculent precipitate persists.)

Add a drop of phenolphthalein and 10% NaCN until pink, then 10 ml. in excess. Dilute to 200 ml. Stir and let settle. Filter $PbCO_3$ and wash with 1% NaCN until Hg free. Precipitate HgS by passing H_2S for about 5 minutes then heat to 60° C., continue H_2S for 5 minutes more, and let settle.

Prepare a Gooch with a thin asbestos floor, wash with 10% NaCN, HCl (1 : 2) and finally with H_2O, then heat and weigh. Decant the clear liquid into the Gooch with gentle suction and finally transfer the sulfide with acidulated H_2S water. Purify the sulfides by washing with cold HCl (1 : 2), then wash with alcohol and dry.

Purify with CS_2 and alcohol, then dry to constant weight at 100° C. Volatalize HgS and reweigh. Calculate Hg from loss.

NOTES.—If there are more than a few milligrams of nonvolatile, or for exceptionally accurate results, this nonvolatile residue should be redetermined as the sulfide in the same manner as above.

The usual run of battery zincs contain sufficient lead to absorb the mercury, otherwise the zinc must be plated with lead by the addition of sufficient soluble lead salt prior to dissolving with HCl.

DETERMINATION OF MERCURY IN CYANIDE SOLUTIONS AND IN CYANIDE PRECIPITATES

The procedure as recommended by W. J. Sharwood (Mining Sci. Press, Oct. 30, 1915) is as follows:

Measure 1000 ml. of solution into a 2500 ml. acid-bottle, give the contents a rotary motion and add half a gram of the finest aluminum powder. Shake the bottle violently for half a minute, then give it a rapid rotary motion and allow to stand for a half to one minute; by this means the solution continues moving most of the time. Repeat the violent shaking, etc., at least 6 times—a total of 5 to 10 minutes. Meanwhile prepare a porcelain Gooch crucible, covering the perforated bottom with a layer of fine asbestos, and connect with an empty 2500 ml. bottle attached to a good vacuum-pump. Shake the solution again and pour it all through a large funnel into a 1000 ml. narrow-necked flask. Rinse the bottle twice with a little water and catch the washings in a small beaker. Pour the washings into the flask until nearly full, and pour the remainder upon the Gooch filter. Invert the flask over the filter with the mouth at least half an inch below the rim, clamp it in that position, and then allow the liquid to filter, using a good vacuum. It may require two or three hours to pass through. Remove the empty flask, rinse any adhering particles into a beaker, and transfer to the filter. Wash once with distilled water. When sucked dry, wash once with alcohol, using a pipette to rinse down the sides of the crucible; when drained, wash twice with a little ether to remove any oil, etc. Remove the crucible and heat gently till thoroughly dry; transfer the asbestos filter-pad and contents to the mercury apparatus with a weighed gold foil, and proceed exactly as with ores. See procedure on page 578 "Determining Mercury as a Metal-Amalgamation Method."

Using 1000 ml. of solution, every milligram found corresponds to one part per million, and half a milligram of mercury is easily visible on gold foil. If the solution is very low in alkali and in cyanide a gram of caustic soda may be added; much more is undesirable. In case of doubt there is no harm done by using additional aluminum powder.

Zinc-dust is not a satisfactory substitute for aluminum; the excess of zinc must be removed by hydrochloric acid, and the cadmium it contains also interferes.

In Cyanide Precipitate.—The precipitate, obtained by treatment of cyanide solution with zinc-dust or shaving, may contain mercury in the metallic state or as sulfide.

Metallic mercury probably exists mainly as amalgam, in combination with gold or silver, or with unaltered metallic zinc. Sulfuric acid refining leaves both mercuric sulfide and the metal in the residue.

In using the apparatus for collecting mercury upon silver foil, the quantity of material taken for analysis should not contain over 0.10 g. of mercury, and preferably 0.025 to 0.050 g. From 1 to 2 g. of precipitate is usually a safe amount, but some slime and concentrate precipitates have yielded over 10% mercury when raw, and considerably more after acid refining.

Place the weighed sample in a 150-ml. beaker with watch-glass cover, moisten, and add 10 or 15 ml. dilute hydrochloric acid. When action slackens add more acid and finally heat gently until action ceases. All the lime, practically all the zinc and cadmium, and some copper and lead pass into solution. Dilute with warm water, stir, and allow to settle, and pass the clear liquid through an asbestos Gooch filter, using gentle suction. Heat the residue with a little more acid, dilute and filter as before; finally transfer all the residue to the filter and wash with hot water till all chlorides are removed. The filtrate may be used for the determination of calcium and zinc, and for cadmium if the residue has been thoroughly extracted with acid.

The residue contains all the mercury. As soon as it is sucked dry, wash once with about 10 ml. of alcohol (denatured may be used), using a pipette to rinse the sides of the Gooch crucible; then wash at least twice with ether to remove grease, asphaltum, etc. These washings are discarded unless the organic matter extracted is to be determined by evaporation in a watch-glass. Disconnect the Gooch crucible and dry it in an oven or on a hot plate, avoiding a high temperature. Transfer the asbestos mat and residue to the mercury apparatus with a weighed disk of silver or gold foil. Wipe out the Gooch with a wisp of dry asbestos and add to the residue in the retort. Add 5 g. clean iron-filing or crushed steel and a little well-burned quicklime, and grind up with the residue, using a stout glass rod. Cover with 2 or 3 g. of iron or lime. Clamp foil and cooler upon retort, heat for about 20 minutes, etc., exactly as with ores, and weigh the foil with condensed mercury.

MOLYBDENUM[1]

Mo, *at.wt.* 96.0; *sp.gr.* 10.2; *m.p.* 2620° C.; *oxides*, Mo_2O_3, MoO_3, MoO_2

Molybdenum frequently occurs in granite in the form of sulfide, molybdenite; it is associated as molybdate with iron, lead and calcium. The commercial minerals are molybdenite, MoS_2; wulfenite, $PbMoO_4$. Molybdenite is a bluish gray mineral with metallic lustre, opaque, foliated masses or scales like graphite, easily separated and soft, streak bluish. Wulfenite is a yellow to orange-red mineral with resinous lustre. It may contain vanadium, chromium, arsenic and tungsten. Molybdite is an earthy yellow mineral, opaque to translucent, streak yellow. It is an alteration product of molybdenite, occurring in small proportions with it and is not a commercial ore.

DETECTION

Molybdenum appears in the hydrogen sulfide group; it is precipitated from acid solution by H_2S as a dark brown sulfide, mostly MoS_3. The sulfide is dissolved by digestion with alkali or ammonium sulfides, forming thio-molybdates which impart a deep brown-red color to the solution. In the formation of soluble thio-salts it behaves like arsenic, tin and antimony, but the thio-molybdates of these metals are not deeply colored. When acid solutions of molybdenum are treated with metallic zinc, molybdenum is reduced to a lower valence, imparting various colors to the liquid as reduction progresses. It remains in solution, whereas tin and antimony, if present in the liquid, are reduced to metals. Arsenic, if present, is in part eliminated as arsine. Neither tin, antimony nor arsenic give colored solutions upon reduction with zinc.

Sodium thiosulfate added to a slightly acid solution of ammonium molybdate produces a blue precipitate with a supernatant blue solution. With more acid a brown precipitate is formed.

Sulfur dioxide produces a bluish-green precipitate if sufficient molybdenum is present, or a colored solution with small amounts.

[1] The mineral molybdenite, MoS_2, was for a long time considered to be graphite, which it strongly resembles. Scheele proved it to be an independent substance. The metal is employed in alloy steels, being added to the steel in form of ferromolybdenum or $CaMoO_4$. It is employed in high-temperature resistor furnaces, in supports for tungsten filaments in lamps, and in dentistry for tooth plugs. Ammonium molybdate is valuable in the analytical laboratory for determination of phosphorus.

Molybdenum present as molybdate is precipitated by *disodium phosphate* as yellow ammonium phosphomolybdate from a nitric acid solution. The precipitate is soluble in ammonium hydroxide.

A pinch of powdered mineral on a porcelain lid, moistened with a few drops of *conc. sulfuric acid*, stirred and heated to fumes, then cooled, will produce a blue color when breathed upon. The color disappears on heating, but reappears on cooling. Water destroys the color.

Molybdenite is very similar to graphite in appearance. It is distinguished from it by the fact that nitric acid reacts with molybdenite, MoS_2, leaving a white residue, but has no action upon graphite. The blowpipe gives SO_2 with molybdenite and CO_2 with graphite.

ESTIMATION

The determination is required in the analysis of molybdenum ores; also in iron and copper ores containing molybdenum.

The metal is determined in certain steels and alloys.

The reagents ammonium molybdate and the oxide-molybdic acid, MoO_3 are valuable for analytical purposes. Tests of their purity may be required.

Molybdenum is precipitated from acid solution as sulfide by H_2S, soluble in alkalies. If it is not thrown out with the hydrogen sulfide group it will remain in solution and pass into the soluble alkali group and probably escape detection.

The ores are easily decomposed by acids or by alkali fusion. Details follow later.

PREPARATION AND SOLUTION OF THE SAMPLE

In dissolving the substance the following facts should be kept in mind: The metal is easily soluble in aqua regia; soluble in hot concentrated sulfuric acid, soluble in dilute nitric acid, oxidized by excess to MoO_3. It is dissolved by fusion with sodium carbonate and potassium nitrate mixture. It is insoluble in hydrochloric, hydrofluoric and dilute sulfuric acids.

The oxide MoO_3 is but slightly soluble in acids; soluble in alkalies; MoO_2 is insoluble in hydrochloric and hydrofluoric acids. MoO_3, as ordinarily precipitated, is soluble in inorganic acids and in alkalies. The oxide sublimed is difficultly soluble.

Molybdates of the heavy metals are insoluble in water, the alkali molybdates are soluble.

Ores.—Molybdenum ores are decomposed by fusion with a mixture of sodium carbonate and potassium nitrate, or with sodium peroxide, in an iron crucible, 0.5 gram of the sample being taken and 10 times its weight of fusion mixture. The melt is disintegrated with about 150 ml. of water, the alkali partly neutralized with NH_4Cl and filtered. The molybdenum is in the filtrate, the iron remains in the residue.

It is advisable to dissolve the residue in a little dilute HCl, pour this solution into a hot solution of an excess of NaOH and again filter off the iron hydroxide, adding the filtrate to the first lot.

The combined filtrates and washings are treated with about 5 ml. of a 50% tartaric acid solution or its equivalent in crystals. (This prevents W and V from separating out) and the solution saturated with H_2S. The thiomolybdate solution is made slightly acid with H_2SO_4 (1 : 2) and MoS_3 precipitates.

Steel and Iron.—One to two grams of the drillings are dissolved, a mixture of 25 ml. HCl and 2 ml. HNO_3, additional HNO_3 (1 : 1) being added to oxidize the iron, if necessary. ($KClO_3$ crystals may be used.) A large excess of the oxidizing agent is to be avoided. The solution is evaporated to near dryness and the pasty residue taken up with about 25 ml. water and 10 ml. HCl, and gently heated. A yellow residue is due to WO_3.* This is removed by filtration, and washed. The filtrate contains the molybdenum. This is now treated according to the procedure given under " Separations " for removal of iron.

SEPARATIONS

Separation of Molybdenum from Iron.—The solution containing the molybdenum is treated very cautiously with 2 N NaOH solution to neutralize the greater part of the free acid, but not with such an amount that would color the solution red. The yellow solution is heated to boiling.

In a separate vessel is placed 2 N NaOH in sufficient quantity to combine with all the iron of the sample and about 100% excess (1 ml. of 2 N NaOH =.035 g. Fe); 125 ml. should be sufficient. This solution is heated to boiling and to it is added the hot solution containing the molybdenum. The sample should be added very slowly, preferably through a special funnel with capillary tube, stirring the solution vigorously during the addition. With care a complete separation of iron, free from molybdenum, may be effected, the molybdenum remaining in solution. The mixture is transferred to a 500-ml. volumetric flask.

The volume is made up to exactly 500 ml. and the precipitate allowed to settle. A portion is now filtered off, the first 5–10 ml. being rejected and the following 250 ml. of filtrate is retained for analysis of molybdenum.

Separation of Molybdenum from Iron and the Other Elements commonly present in Steels.[2]

Knowles found that α-Benzoinoxime precipitates molybdenum from solutions containing as much as 20% by volume of H_2SO_4 or 5% by volume of either HCl or HNO_3 or H_3PO_4. The only other elements precipitated in mineral acid solutions by the reagent are Cb, W, Pd, Cr^{VI}, V^{V}, and Ta. The reagent

* The WO_3 will contain some molybdenum.
[2] H. B. Knowles, Bur. Standards J. Research, 9, 1 (1932).

is, therefore, very useful for the determination of molybdenum in steel and in other alloys, and will undoubtedly be found useful in many fields of analysis.

Separation from the Alkaline Earths.—Fusion of the substance with sodium carbonate and extraction of the melt with water gives a solution of molybdenum, whereas the carbonates of barium, calcium and strontium remain undissolved.

Separation from Lead, Copper, Cadmium and Bismuth.—The sulfides of the elements are treated with sodium hydroxide and sodium sulfide solution and are digested by gently heating in a pressure flask. Molybdenum dissolves, whereas lead, copper, cadmium and bismuth remain insoluble. If the solution of the above elements is taken, made strongly alkaline, and treated with H_2S, the sulfides of the latter elements are precipitated and molybdenum remains in solution. The precipitates are filtered off and the filtrate containing molybdenum is made slightly acid with sulfuric acid and the mixture heated, until the liquid appears colorless, MoS_3 is precipitated and may be converted into the oxide as described later.

Separation of Molybdenum from Iron, Aluminum, Chromium, Nickel, Cobalt, Zinc, Manganese, Alkaline Earths and Alkalies.—Molybdenum is precipitated from an acid solution, preferably a mixture of H_2SO_4 and HCl—1 and 2 ml. respectively in a volume of 50 ml. After saturating with H_2S, the solution is diluted with an equal volume of water and again saturated with H_2S and the sulfides filtered and washed as usual. Members of the H_2S group will be present, if in the original solution.

Separation from Vanadium is effected by a molybdenum sulfide precipitation in acid solution.

Separation from Arsenic.—(*a*) Arsenic, present in the higher state of oxidation, is precipitated by magnesia mixture, added to a slightly acid solution (5 ml. of concentrated hydrochloric acid per 100 ml. of solution for each 0.1 gram arsenic). The solution is neutralized with ammonia (methyl orange), and the arsenic salt filtered off. MoS_3 is now precipitated with H_2S in presence of free sulfuric acid in the pressure flask. (*b*) Arsenic is reduced to arsenous form and distilled as $AsCl_3$ separating it from molybdenum.

Separation from Phosphoric Acid.—Phosphoric acid is precipitated from an ammoniacal solution as magnesium ammonium phosphate. Molybdenum may then be precipitated as the sulfide from the filtrate.

Separation from Titanium.—Ammonia will separate molybdenum from titanium. The metals of the ammonium sulfide group and titanium are precipitated by adding ammonium hydroxide and ammonium sulfide. Molybdenum remains in solution and passes into the filtrate. H_2S is passed into the solution until it appears red; sulfuric acid is then added until the solution is acid, when molybdenum sulfide precipitates.

Separation from Tungsten.—Molybdenum may be precipitated by H_2S as MoS_3 in presence of tartaric acid. Tungsten does not precipitate.

MoS_3 may be precipitated from a formic acid solution by H_2S, tungsten remains in solution.[3] The alkaline solution is neutralized with concentrated formic acid and an excess of ammonium sulfide added followed by more formic acid with 5 ml. excess per each 100 ml. of solution. After standing for half an hour or more the MoS_3 is filtered off and washed with a 5% solution of formic acid.

[3] J. Sterba Böhm and J. Vostrebal, Z. anorg. allgem. chem., 110, 81, 1920.

Ether Extraction Method.—Ether extracts not only iron but also molybdenum (see p. 465). The ether is evaporated off on a steam bath (avoid a free flame, as ether is inflammable) and the solution taken to near dryness. Ten ml. of sulfuric acid are added and hydrochloric acid expelled by concentration to fumes. After cooling, 100 ml. of water are added and 2–3 grams of ammonium bisulfite, to reduce the iron. The solution is boiled to expel the excess of SO_2 and molybdenum is precipitated by H_2S, in a pressure flask. After cooling slowly, the sulfide, MoS_2, is filtered off, washed and ignited and weighed as MoO_3

GRAVIMETRIC METHODS FOR THE DETERMINATION OF MOLYBDENUM

PRECIPITATION AS LEAD MOLYBDATE

Preliminary Remarks.—This method, suggested by Chatard,[4] has been pronounced by Brearly and Ibbotson to be " one of the most stable processes found in analytical chemistry." " It is not interfered with by the presence of large amounts of acetic acid, lead acetate, or alkali salts (except sulfates). The paper need not be ignited separately and prolonged ignition at a much higher temperature than is necessary to destroy the paper does no harm. From faintly acid solution lead molybdate may be precipitated free from impurities in the presence of copper, cobalt, nickel, manganese, zinc, magnesium and mercury salts." It may be readily separated from coprecipitated iron and chromium. Barium, strontium, uranium, arsenic, cadmium and aluminum do not interfere if an excess of hydrochloric acid has been added to the solution followed by lead acetate and sufficient ammonium acetate to destroy the free mineral acid.

The method is not adapted to use with molybdenite, MoS_2, because of the sulfate that forms on oxidation.

Vanadium and tungsten, if present, must be removed. Fe, Cr, Si, Sn, Ti, Bi, Sb will contaminate the precipitate if present.

Special Reagents. ***Lead Acetate.***—A 4% solution is made by dissolving 20 grams of the salt in 500 ml. of warm water. A few ml. of acetic acid are added to clear the solution.

Precipitation of Lead Molybdate.—The solution acidified with acetic acid (5 ml. per 200 ml.) and free from iron, is heated to near boiling and the lead acetate reagent added slowly until no further precipitation occurs and then

[4] T. M. Chatard, Am. J. Sci. (3), 1, 416, 1871.

about 5% excess. (One ml. of the 4% lead acetate reagent will precipitate about 0.01 gram of molybdenum.) The precipitate is allowed to settle a few minutes and filtered hot into a weighed Gooch crucible or into a filter paper. (Refiltering first portion if cloudy.)[5] The precipitate is washed with hot water until free of chlorides and the excess of the lead acetate.

The precipitate dried and ignited in a porcelain crucible at red heat for about twenty minutes is weighed as $PbMoO_4$.

$$PbMoO_4 \times 0.2614 = Mo. \quad PbMoO_4 \times 0.3922 = MoO_3.$$

$$Mo \times 3.8255 = PbMoO_4. \quad MoO_3 \times 2.550 = PbMoO_4.$$

PRECIPITATION AND WEIGHING AS SILVER MOLYBDATE

Silver molybdate is an excellent form in which to precipitate and weigh molybdate. The procedure is useful for standardization of solutions of molybdenum and for checking the amount of MoO_3 extracted by ammonia from the crude oxide as obtained in many analytical procedures.[6] 100 ml. of water dissolved 0.0044 g. Ag_2MoO_4 at 25°, but the precipitate is practically insoluble when an excess of silver is present. The latter may be washed out with alcohol.

Procedure.—To 150 ml. of the ammonium or other alkali molybdate solution is added a drop of methyl orange and enough sulfuric acid to change the color to red. One g. of $NaC_2H_3O_2 \cdot 3H_2O$ is dissolved in the solution; heat to boiling and add $AgNO_3$ solution to complete precipitation. The precipitate is filtered on a filter crucible, washed with a solution of 5 g. $AgNO_3$ per 1000 ml. of H_2O. The excess of $AgNO_3$ is removed by C_2H_5OH; wash with three 5 ml. portions of C_2H_5OH (95%). Dry the precipitate to constant weight at 250° C.

A. DETERMINATION OF MOLYBDENUM AS THE OXIDE, MoO_3

Separation as Mercurous Molybdate

Especially applicable for small amounts of molybdenum where fusion with an alkali carbonate has been required.

Decomposition of Ore.—One gram of the ore is fused with 4 grams of fusion mixture, ($Na_2CO_3 + K_2CO_3 + KNO_3$), and the cooled melt extracted with hot water.

If *manganese is present*, indicated by a colored solution, it may be removed by reduction with alcohol, the manganese precipitate filtered off and washed with hot water, the solution evaporated to near dryness and taken up with water, upon addition of nitric acid as stated below.

The solution containing the alkaline molybdate is nearly neutralized by adding HNO_3, the amount necessary being determined by a blank, and to the cold, slightly alkaline solution, a faintly acid solution of mercurous nitrate is added until no further precipitation occurs. The precipitate consists of mer-

[5] Addition of ammonium nitrate to the solution tends to prevent formation of colloidal $PbMoO_4$. Paper pulp (ashless) may be added to assist rapid filtration.

[6] L. W. McCay, J. Am. Chem. Soc., 56, 2548 (1934).

curous molybdate and carbonate (chromium, vanadium, tungsten, arsenic and phosphorus will also be precipitated if present). The solution containing the precipitate is boiled and allowed to stand ten to fifteen minutes to settle, the black precipitate is filtered off and washed with a dilute solution of mercurous nitrate. The precipitate is dried, and as much as possible transferred to a watch-glass. The residue on the filter is dissolved with hot dilute nitric acid, and the solution received in a large weighed porcelain crucible. The solution is evaporated to dryness on the water bath and the main portion of the precipitate added to this residue, and that product heated cautiously over a low flame [7] until the mercury has completely volatilized. The cooled residue is weighed as MoO_3.

$$MoO_3 \times 0.6667 = Mo.$$

NOTE.—If Cr, V, W, As or P are present a separation must be effected. Molybdenum should be precipitated in an H_2SO_4 solution in a pressure flask as the sulfide by H_2S as given in the following method, and arsenic if present removed by magnesia mixture as indicated in the procedure for separation of arsenic from molybdenum. If these impurities are present the molybdenum oxide may be fused with a very little Na_2CO_3, and leached with hot water and the filtrate treated with H_2S as directed.

SEPARATIONS AS THE SALT OF α-BENZOINOXIME [8]

Procedure Recommended for General Use.—Prepare a solution containing 10 ml. of sulfuric acid (specific gravity 1.84) in a volume of 200 ml. and not more than 0.15 g. of sexivalent molybdenum. If vanadates or chromates are present add sufficient freshly prepared sulfurous acid to reduce them and heat to boiling. Continue the boiling until the odor of sulfur dioxide can no longer be detected. Chill the solution to a temperature of 5° to 10° C. Stir and slowly add 10 ml. of a solution of 2 g. of α-benzoinoxime in 100 ml. of alcohol and 5 ml. extra for each 0.01 g. of molybdenum present. Continue to stir the solution, add just sufficient bromine water to tint the solution a pale yellow and then add a few milliliters of the reagent. Allow the beaker and contents to remain in the cooling mixture 10 to 15 minutes with occasional stirring, stir in a little macerated filter pulp and filter through a paper of close texture, such as S. & S. No. 589 Blue Band. Filtration can be greatly facilitated by using a coarser filter, such as S. & S. No. 589 Black Band, but it is then requisite that the filtrate be very carefully examined and the first portions refiltered if they are not absolutely clear. Wash the precipitate with 200 ml. of a cold, freshly prepared solution containing 25 to 50 ml. of the prepared reagent and 10 ml. of sulfuric acid in 1000 ml. On standing, the filtrate will deposit needle-like crystals if sufficient reagent has been employed.

Transfer the washed precipitate to a weighed platinum crucible, cautiously dry; char, without flaming, over a very low gas flame and then ignite to constant weight in an electric muffle at 500° to 525° C. In umpire analyses of materials containing silica it is best to remove that constituent before proceeding with the precipitation of molybdenum rather than to treat the final precipitate with sulfuric and hydrofluoric acids, because of the uncertainty of completely decomposing molybdenum sulfate at the temperature of ignition.

[7] The oxide, MoO_3, sublimes at bright red heat. At 500–550° C. the loss is only 0.1 mg. per hour. M. P. Brinton and A. F. Stoppel, J. Am. Chem. Soc., 46, 2454, 1924.
[8] H. B. Knowles, Bur. Standards J. Research, 9, 1 (1932).

If the oxide contains no impurities, except tungsten, it should dissolve completely in warm dilute ammonium hydroxide. If an insoluble residue remains, it must be separated by filtration, ignited, weighed, and the weight subtracted.

The method may be applied to the determination of Mo in molybdenite and wolfenite. The ore is brought into the solution in nitric acid (sp.gr. 1.42) and bromine. It is then treated with 25 ml. of diluted H_2SO_4 (1 : 1) and evaporated to fumes of SO_3 after the addition of 100 ml. of water, heating to dissolve soluble sulfates; filter, and wash with sulfuric acid (2 : 100). The molybdenum is determined colorimetrically in the insoluble residue after fusion, etc. The filtrate is diluted to 200 ml., treated with 0.1 N $KMnO_4$ to a permanent pink tinge to complete the oxidation of the molybdenum. Fresh H_2SO_3 is added to reduce V^{v} and Cr^{vi}. The excess of SO_2 is boiled out. After cooling, the molybdenum is precipitated by excess of benzoinoxime, and the precipitate is filtered, washed, dried, ignited, and weighed.

The ignited oxide is dissolved in a minimum of warm dil. NH_4OH, filtered, washed, and weighed. The extract containing the molybdenum is acidified with HCl, treated with cinchonine, digested over night, and any precipitate of W is filtered, washed, ignited at 570° C., and weighed. The weight of this residue and of that insoluble in NH_4OH is deducted from the weight of the crude MoO_3.

B. DETERMINATION AS THE OXIDE MoO_3

Separation of Molybdenum as the Sulfide by H_2S

A. **Precipitation from Acid Solution.**—By this procedure molybdenum is precipitated along with members of the hydrogen sulfide group, if present, but free from elements of the following groups.

The cold molybdenum solution slightly acid with sulfuric acid (in presence of Ba, Sr or Ca an HCl solution is necessary) is placed in a small pressure flask and saturated with H_2S, the flask closed and heated on the water bath until the precipitate has settled. The solution is cooled and filtered through a weighed Gooch crucible.

B. **Precipitation from an Ammoniacal Solution.**—By this procedure molybdenum is precipitated with antimony, arsenic and tin, if present, but is free from mercury, lead, bismuth, copper and cadmium.

Hydrogen sulfide is passed into the cold ammoniacal solution of molybdenum (in presence of tungsten or vanadium add tartaric acid) until it assumes a bright red color, it is now acidified with dilute sulfuric acid, heated to boiling, the precipitate allowed to settle and the solution filtered through a weighed Gooch crucible.

In either case A or B the precipitate is washed into the Gooch crucible with very dilute sulfuric acid followed by several washings with the acid and then with alcohol until free from acid. The Gooch is placed within a larger nickel crucible and covered with a porcelain lid. After drying at 100° C. it is placed over a small flame and carefully heated until the odor of SO_2 can no longer be detected. The cover is now removed and the open crucible heated to constant weight at 525° C. The residue consists of MoO_3.

$$MoO_3 \times 0.6667 = Mo.$$

NOTE.—Arsenic will contaminate the residue if present. The method for its removal has been given.

SEPARATION OF MOLYBDENUM FROM TUNGSTEN [9]

Procedure.—To a solution of sodium tungstate and sodium molybdate in 10–15 ml. is added 10 ml. of 50% ammonium formate, 10 ml. of 30% tartaric acid and 100 ml. of water saturated at zero with H_2S, and 10 ml. of 2 M formic acid. At this point, the solution has a pH of 2.9. Heat the mixture at 60° C. on a water bath for one hour, having a flask stoppered with a one-hole stopper, the outlet of which is closed with a glass ball held in place by a stout rubber band. The stopper is also held in place by a second rubber band which is carried around the bottom of the flask. Add a small quantity of filter paper pulp and add 10 ml. of 24 M formic acid to complete the precipitation of the molybdenum sulfide. Keep the mixture at 60° for thirty minutes longer, filter through a Gooch or porcelain filter and crucible, and wash the precipitate with 5–10 ml. portions of a mixture of 5 ml. 50% ammonium formate, 5 ml. of 24 M formic acid and 100 ml. of water. The molybdenum sulfide is converted to the oxide in an electric oven at a temperature of 500–550° C.

The filtrate is concentrated and treated with 25 ml. of 16 M HNO_3. The ammonium salts are destroyed by evaporation and the precipitation of the WO_3 is completed using the customary cinchonine reagent. The WO_3 is brought to constant weight by heatings at a final temperature of 750° in an electric oven.

VOLUMETRIC METHODS FOR THE DETERMINATION OF MOLYBDENUM OR MOLYBDIC ACID

THE IODOMETRIC REDUCTION METHOD [10]

Principle.—When a mixture of molybdic acid and potassium iodide in presence of hydrochloric acid is boiled, the volume having defined limits, free iodine is liberated and expelled and the molybdic acid reduced to a definite lower oxide; by titrating with a standard oxidizing agent the molybdic acid is determined.

Reaction.—$2MoO_3+4KI+4HCl=2MoO_2I+I_2+4KCl+2H_2O$.

Reagents.—N/10 solutions of iodine, sodium arsenite, potassium permanganate, sodium thiosulfate.

Analytical Procedure.[11] **Reduction.**—The soluble molybdate in amount not exceeding an equivalent of 0.5 gram MoO_3 is placed in a 150-ml. Erlenmeyer

[9] Yagoda and Fales, J. Am. Chem. Soc., 58, 1494 (1936).
[10] F. A. Gooch and Charlotte Fairbanks, Am. J. Sci. (4), 2, 160 (1896).
[11] F. A. Gooch and O. S. Pulman, Jr., Am. J. Sci. (4), 12, 449 (1901).

flask, 20 to 25 ml. of hydrochloric acid (sp.gr. 1.19) added together with 0.2 to 0.6 gram potassium iodide. A short stemmed-funnel is placed in the neck of the flask to prevent mechanical loss during the boiling. The volume of the solution should be about 600 ml. The solution is boiled until the volume is reduced to exactly 25 ml. as determined by a mark on the flask. The residue is diluted immediately to a volume of 125 ml. and cooled. Either process *A* or *B* may now be followed.

A. **Reoxidation by Standard Iodine.**—A solution of tartaric acid, equivalent to 1 gram of the solid, is now added, and the free acid nearly neutralized with sodium hydroxide solution (litmus or methyl orange indicator) and finally neutralized with sodium acid carbonate, $NaHCO_3$, added in excess. A measured amount of N/10 iodine is now run in. The solution is set aside in a dark closet for two hours, in order to cause complete oxidation, as the reaction is slow. The excess iodine is now titrated with N/10 sodium arsenite.

One ml. N/10 iodine = .0144 gram MoO_3 = .0096 gram Mo.

On long standing a small amount of iodate is apt to form. This is determined by making acid with dilute HCl and titrating with N/10 sodium thiosulfate.

B. **Reoxidation of the Residue by Standard Permanganate.**—To the reduced solution about 0.5 gram of manganese sulfate in solution is added, followed by a measured amount of N/10 permanganate solution, added from a burette until the characteristic pink color appears. A measured amount of standard N/10 sodium arsenite, equivalent to the permanganate is then run in and about 3 grams of tartaric acid added. The acid is neutralized by acid sodium or potassium carbonate, the stopper and the sides of the flask rinsed into the main solution. The residual arsenite is now titrated by N/10 iodine, using starch indicator.

NOTES.—Tartaric acid prevents precipitation during the subsequent neutralization with $NaHCO_3$. *A* and *B*.

The addition of manganese salt in *B* is to prevent the liberation of free chlorine by the action of $KMnO_4$ on HCl.

In addition to the oxidation of the lower oxides to molybdic acid, potassium permanganate added in *B* liberates free iodine from HI, it produces iodic acid, and forms the higher oxides of manganese. The standard arsenite, on the other hand, converts free iodine and the iodate to HI and reduces the higher oxides of manganese.

ESTIMATION BY REDUCTION WITH JONES REDUCTOR AND OXIDATION BY STANDARD PERMANGANATE SOLUTION

Principle.—The procedure depends upon the reduction of sexivalent molybdenum to the trivalent form by passing its acidified solution through a column of amalgamated zinc. Since the reduced molybdenum compound is sensitive to the oxygen of the air, resulting in partial oxidation,[12] the reduced compound is caught in an excess of ferric solution, whereupon an equivalent amount of ferric compound is reduced to ferrous state. Titration of the

[12] D. L. Randall, Am. J. Sci. (4), 24, 313, 1907.

reduced iron by means of standard potassium permanganate establishes the amount of molybdenum reduced by the zinc.

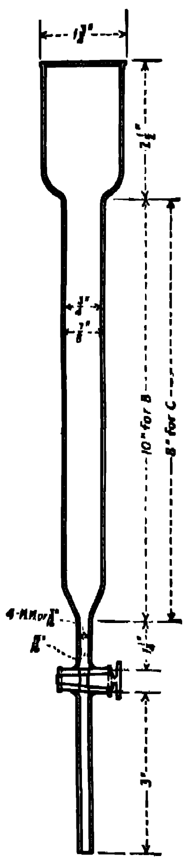
$$2MoO_3 \rightarrow Mo_2O_3; \quad \text{and} \quad Mo_2O_3 + 3Fe_2O_3 \rightarrow 6FeO + \text{oxidized Mo.}$$
$$Mo = 3Fe.$$

Reagents.—*Potassium permanganate* approximately N/10 standardized against pure sodium oxalate.

10% solution of *ferric alum.*

2.5% solution of *sulfuric acid.*

Apparatus.—*Jones Reductor.*



R = reductor tube 50 cm. long, 2 cm. inside diameter. Smaller tube prolongation length 20 cm. inside diameter 0.5 cm.;
Zn = column of zinc 40 cm. long. Zn shot 8 mesh to sq.cm.;
F = receiving flask;
P = pressure regulator with gauge, set to give pressure in receiving flask of less than 20 cm. water;
G = platinum cone or gauze with mat of fine glass wool 2 cm. thick;

The zinc in reductor should be protected from the air by covering with water, stopcock S being closed when not in use.

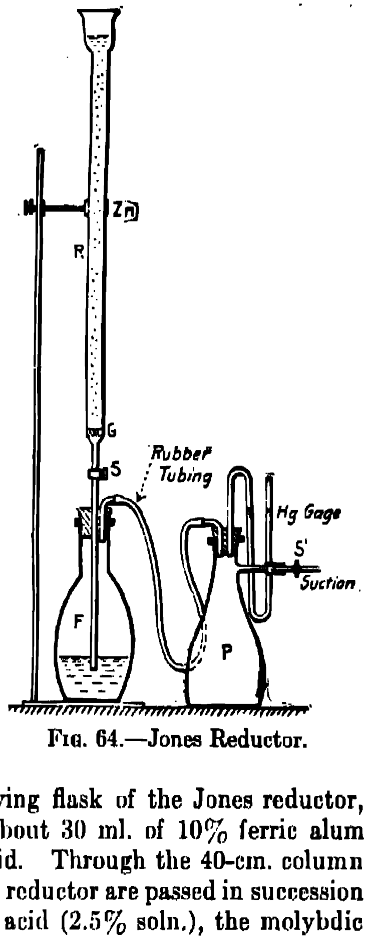


Fig. 64.—Jones Reductor.

Procedure.—The receiving flask of the Jones reductor, Fig. 64, is charged with about 30 ml. of 10% ferric alum and 4 ml. of phosphoric acid. Through the 40-cm. column of amalgamated zinc in the reductor are passed in succession 100 ml. of dilute sulfuric acid (2.5% soln.), the molybdic acid in the form of ammonium molybdate dissolved in 10 ml. of water and acidified with 100 ml. of dilute sulfuric acid followed by 200 ml. more of the dilute sulfuric acid and 100 ml. of water. The reduced green molybdic acid upon coming in contact with the ferric alum solution produces a bright red color.

Fig. 65.—Reductor Tube.

The solution is titrated with N/10 $KMnO_4$ solution.

$$\text{One ml. of N/10 } KMnO_4 = \frac{.0144}{3} \text{ gram } MoO_3 = \frac{.0096}{3} \text{ gram molybdenum.}$$

Notes.—Substances reduced by zinc and oxidized by $KMnO_4$ should be absent, i.e. organic matter, HNO_3, compounds of As, Sb, Cb, Cr, Fe, Ti, V, U and W. Organic matter and HNO_3 are removed by taking to fumes with H_2SO_4, the remainder are sepa-

rated by the following treatment:—An excess of ferric iron is added and a double precipitation is made with NH_4OH, the filtrate containing Mo and W is treated with tartaric acid and H_2S and filtered. The filtrate is acidified and saturated with H_2S, molybdenum precipitates free from interfering substances. Consult section on Separations.

The ferric salt should be in large excess of that required theoretically in the oxidation of Mo_2O_3 to 2 MoO_3.

REDUCTION WITH MERCURY[13]

The molybdenum solution is made 3 N (approx.) in HCl and is shaken vigorously with 25 ml. of mercury in a glass-stoppered vessel. The reduced solution is filtered to remove calomel and 1 : 5 HCl is used for washing the latter, and the Mo^V is titrated with standard ceric sulfate using o-phenanthroline indicator (2 drops of 0.025 M indicator are used, and the volume must be 300 ml. if 0.25 g. of Mo are present before adding the indicator). As much as 0.25 g. of either phosphate or arsenate does not interfere. The acidity of the solution must not be as high as 4 N in HCl during the reduction because partial reduction to Mo^{III} occurs at acidities of 4 N and higher. Copper, even in quantities of the order of 0.1–1 mg. causes serious interference by catalyzing the autoxidation of the reduced solution by air. The copper must be excluded, or alternatively oxygen must be excluded.

Ceric sulfate may also be used for the titration of the ferrous solution produced when Mo^{III} is led from a Jones reductor into an excess of ferric sulfate.

METHOD FOR DETERMINING MOLYBDENUM AND VANADIUM IN A MIXTURE OF THEIR ACIDS

Principle of the Method.—The procedure depends upon the fact that vanadic acid alone is reduced by SO_2[14] in a sulfuric acid solution, whereas both vanadic and molybdic acids are reduced by amalgamated zinc, in each case the reducing agents forming definite lower oxides which are readily oxidized to definite higher oxides by $KMnO_4$.

Reactions.

SO_2 Reduction:

1. $V_2O_5+SO_2=V_2O_4+SO_3$. (No action on MoO_3.)

Zn Reduction:

2. $V_2O_5+3Zn=V_2O_2+3ZnO$.
3. $2MoO_3+3Zn=Mo_2O_3+3ZnO$.

$KMnO_4$ Oxidation:

4. $5V_2O_4+2KMnO_4+3H_2SO_4=5V_2O_5+K_2SO_4+MnSO_4+3H_2O$.
5. $5V_2O_2+6KMnO_4+9H_2SO_4=5V_2O_5+3K_2SO_4+6MnSO_4+9H_2O$.
6. $5Mo_2O_3+6KMnO_4+9H_2SO_4=10MoO_3+3K_2SO_4+6MnSO_4+9H_2O$.

From the reactions " 4 " and " 5 " it is seen that three times the amount of $KMnO_4$ is required to oxidize V_2O_2 to V_2O_5 as is required in the case of V_2O_4,

[13] Furman and Murray, J. Am. Chem. Soc., 58, 1689 (1936).

[14] Reduction of vanadium by SO_2 in presence of molybdenum, Graham Edgar, Am. J. Sci. (4), 25, 332 (1908). No reduction of MoO_3 when 0.4 gram is present with 5 ml. H_2SO_4 in 25 ml. volume.

For theoretical considerations and data on accuracy of method see "Methods in Chemical Analysis," F. A. Gooch.

hence—total ml. $KMnO_4$ required in oxidation of the zinc-reduced oxides minus three times the ml. $KMnO_4$ required in oxidizing the tetroxide of vanadium formed by the sulfur dioxide reduction = ml. $KMnO_4$ required to oxidize Mo_2O_3 to MoO_3. From these data molybdenum and vanadium may readily be calculated.

Method of Procedure. *A.* **Vanadic Acid.**—The solution containing the vanadic and molybdic acids in a 250- to 300-ml. Erlenmeyer flask, is diluted to 75 ml., acidified with 2 to 3 ml. of sulfuric acid, (1.84) heated to boiling and the vanadic acid reduced by a current of SO_2 passed into the solution until the clear blue color indicates the complete reduction of the vanadic acid to V_2O_4. The boiling is now continued and CO_2 passed into the flask to expel the last trace of SO_2.

Standard N/10 $KMnO_4$ is now run into the reduced solution to the characteristic faint pink. From reaction "4," vanadic acid may be calculated.

One ml. N/10 $KMnO_4$ = .00910 gram V_2O_5 = .0051 gram vanadium.

B. **Molybdic Acid.**—The reduction by Jones' reductor, and titration of the combined acids reduced by amalgamated zinc with N/10 potassium permanganate solution, is carried out exactly as described in the determination of molybdic acid alone. In this case 50 ml. of 10% ferric alum and 8 ml. of the phosphoric acid is placed in the receiving flask.

Calculation.—Total permanganate titration in *B* minus three times the titration in *A* gives the permanganate required to oxidize Mo_2O_3 to MoO_3. From equation 6 the molybdic acid may now be calculated.

$$\text{One ml. N/10 } KMnO_4 = \frac{.0144}{3} \text{ gram } MoO_3 = \frac{.0096}{3} \text{ gram molybdenum.}$$

DETERMINATION OF MOLYBDENUM[15]

An amount of the sample sufficient to give a weight of from 0.2 to 0.3 gram of molybdenum is employed. In the case of very pure molybdenite or molybdenite concentrates this will correspond to from 0.5 to 1 gram of sample whereas even with the highest grade wulfenite or wulfenite concentrates it is never advisable to employ less than 1 gram. The accurately weighed sample which has been previously dried for 1 hour at 105° C. is treated with from 10 to 15 ml. of nitric acid (sp.gr. 1.42) and from 7 to 10 ml. of sulfuric acid (sp.gr. 1.84) in a 250-ml. beaker provided with a clock-glass cover, at a temperature somewhat below the boiling point. As much as 4 or 5 grams of ores or tailings, very low in molybdenum, and correspondingly increased amounts of acids are necessary. Wulfenite ores and concentrates can also be decomposed completely by means of concentrated hydrochloric acid followed by evaporation to fumes with sulfuric acid but the use of nitric acid is preferred. The beaker and its contents are heated, with occasional stirring, until the sample appears to have been decomposed completely, when the solution is evaporated cautiously until fumes of sulfur trioxide are expelled freely.

[15] Contributed by Thos. R. Cunningham, Chief Chemist, Union Carbide and Carbon Research Laboratories, Inc.

After having allowed the beaker and its contents to cool somewhat, 50 ml. of water are added and the liquid is stirred and boiled briskly for a few minutes to dissolve all molybdenum and other soluble salts. The next step varies slightly depending upon whether *molybdenite* or *wulfenite* is being analyzed.

In the case of *molybdenite* the hot solution is filtered on a 9 cm. paper into a 150-ml. beaker and the siliceous residue is washed 8–10 times with hot water, 3–4 times with hot dilute (1 : 3) ammonium hydroxide, and finally 4–5 times more with hot water, the washings being allowed to run into the main filtrate. The siliceous residue is as a rule practically free from molybdenum. However, as a precaution it is ignited in a porcelain crucible at a temperature not higher than 450° C., cooled, and transferred to a 30-ml. platinum crucible. One-half (0.5) ml. of sulfuric acid (sp.gr. 1.84), 2 ml. of nitric acid (sp.gr. 1.42) and 5 ml. of hydrofluoric acid are added and the solution is evaporated to strong fumes of sulfur trioxide, and reserved for further treatment.

Due to the fact that *wulfenite* contains lead, a slightly different procedure is followed in its case. The solution is cooled to tap water temperature, filtered on a 9-cm. paper into a 150-ml. beaker, and the residue of silica, lead sulfate, and possibly tungstic acid, is washed thoroughly with cold 2% sulfuric acid. The residue and filter paper are returned to the 150-ml. beaker and digested with 50 ml. of ammonium acetate solution (prepared by mixing 18 ml. of NH_4OH, (sp.gr. 0.90), with 20 ml. of water, and 12 ml. of 99% $HC_2H_3O_2$), at a temperature just short of boiling for about 5 minutes. The solution is filtered on an 11-cm. paper, the paper and residue washed thoroughly with a hot 5% ammonium acetate solution, and ignited in porcelain at a temperature not higher than 525° C., cooled and transferred to a 30-ml. platinum crucible. One-half (0.5) ml. of sulfuric acid (sp.gr. 1.84), 2 ml. of nitric acid (sp.gr. 1.42) and 5 ml. of hydrofluoric acid are added, and the solution is evaporated to strong fumes of sulfur trioxide and reserved for further treatment.

To the solution containing all of the molybdenum there is added sufficient ferric sulfate to provide 10 times as much iron as there is *arsenic* present. This step is usually superfluous in the case of molybdenite, which seldom contains much arsenic, but with wulfenite ores or concentrates, which often carry several per cent of mimetite (lead chloro-arsenate), $(PbCl)Pb_4(AsO_4)_3$, the use of ferric sulfate is absolutely necessary. From 0.3 to 0.4 gram of ferric sulfate is usually ample to insure the retention of all of the arsenic by the ferric hydroxide. Regardless of whether or not iron was added, the acid solution is nearly neutralized with ammonia (addition of an amount sufficient to impart a permanent red tint to the clear yellow solution is to be avoided), heated nearly to boiling, and poured *very slowly and with vigorous stirring* into 75 ml. of nearly boiling 15% ammonium hydroxide contained in a 250-ml. beaker. The precipitate of ferric hydroxide, etc. (which will carry down quantitatively all arsenic in the ore, provided the iron-arsenic ratio is as great as 10 to 1) is filtered on a 9-cm. paper and washed thoroughly with hot water. A second separation is then made by dissolving the precipitate in a *slight* excess of hot dilute (1 : 4) sulfuric acid, again pouring it into 75 ml. of nearly boiling 15% ammonium hydroxide contained in a 250-ml. beaker, and filtering and washing the precipitate as previously described. The two filtrates, which will contain practically all of the molybdenum, are collected in a 600-ml. beaker. The ferric hydroxide

precipitate is dissolved in 15 ml. of hot dilute sulfuric acid (1 : 4) and reserved for further treatment.

It is essential that arsenic, which is almost invariably present in wulfenite, be eliminated, and the method described furnishes a simple and effective way of accomplishing this. Experiments have shown that *in presence of molybdenum* it is very difficult to completely volatilize arsenic by reduction with sulfurous acid and boiling with concentrated hydrochloric acid—a portion is held tenaciously in the solution. In addition to precipitating the arsenic, the ferric hydroxide also carries down most of the *vanadium* and *tungsten* which are ordinary constituents of wulfenite ores.

To the combined ammoniacal filtrates there are added 2 grams of powdered tartaric acid and the warm liquid is saturated thoroughly with a stream of washed hydrogen sulfide. The function of the tartaric acid is to prevent the precipitation of any tungsten or *vanadium* along with the molybdenum; its use should never be omitted in the case of wulfenite, although since molybdenite is usually free from significant amounts of these elements, the amount used in its case may be safely reduced to 1 gram. Under these conditions the molybdenum remains in solution as ammonium thiomolybdate, $(NH_4)_2MoS_4$, which imparts a deep red color to the solution. If a small precipitate of insoluble sulfides separates out, it is filtered off and washed with dilute ammonium sulfide water; if the solution remains clear, this step is omitted. Copper, in the amounts usually present, remains entirely in solution at this point and is reprecipitated with the molybdenum when the solution is subsequently acidified. The thiomolybdate solution is then made slightly acid with sulfuric acid (1 : 2). This results in the precipitation of the molybdenum as trisulfide as shown in the following equations:

$$(NH_4)_2MoS_4 + H_2SO_4 = MoS_3 + H_2S + (NH_4)_2SO_4,$$

$$(NH_4)_2S + H_2SO_4 = H_2S + (NH_4)_2SO_4.$$

The cessation of effervescence on addition of more acid, the absence of the odor of ammonium sulfide and the disappearance of the red color of the ammonium thiomolybdate, mark the point where sufficient acid has been added to complete the reactions.

The beaker and its contents are heated for about 15 minutes at a temperature just short of boiling, the solution filtered on an 11-cm. paper and the precipitate washed thoroughly with hydrogen sulfide water containing a small amount of sulfuric acid.

The slightly acid filtrate from the molybdenum sulfide is boiled to expel free H_2S, when the sulfuric acid solution (contained in the 30-ml. platinum crucible) of the insoluble residue obtained as described in the third or fourth paragraph, and the sulfuric acid solution of the ferric hydroxide precipitate obtained as described in the fifth paragraph, are added, together with 1 ml. of hydrogen peroxide (3%), and the solution further boiled until the volume has been reduced to 50 ml. The solution is transferred to a 250-ml. separatory funnel and cooled to 15° C. The determination for molybdenum is then completed by the colorimetric method. See p. 609.

Any molybdenum found is added to that obtained by passage of the molybdenum solution through the zinc reductor to obtain the total molybdenum in the sample.

The molybdenum sulfide precipitate and paper, or precipitates and papers, are put into a 250-ml. beaker and treated with 6 ml. of sulfuric acid (sp.gr. 1.84) and 10 ml. of nitric acid (sp.gr. 1.42) and the liquid is boiled cautiously until dense fumes of sulfur trioxide are evolved freely. After having allowed the solution to cool somewhat, 5 ml. of nitric acid (sp.gr. 1.42) are added and the evaporation is repeated. The evaporation with 5 ml. portions of conc. nitric acid is repeated several times until the filter paper has been destroyed completely and every trace of yellow color due to carbonaceous matter has disappeared. When this has been accomplished, the solution is fumed strongly for a short while, cooled, 5 ml. of water and several drops of strong permanganate (25 grams per liter) are added, and in order to insure the expulsion of every trace of nitric acid, the liquid is again evaporated to strong fumes of sulfur trioxide. After having allowed the beaker and its contents to cool, approximately 75 ml. of water are introduced and the contents of the beaker are boiled for a few minutes, which should result in a perfectly clear solution being obtained. Two grams of pure shot zinc (0.002% iron or under) are then added and the solution is cooled until most of it has dissolved; this results in partial reduction of the molybdenum and complete precipitation of the copper which is usually present. The liquid is then filtered on an asbestos or "alundum" filter to remove the undissolved zinc and copper.

The next step consists in reducing the molydenum from the sexivalent to the trivalent condition by passage through a zinc reductor in the following manner: The reductor being clean and in good condition from previous treatment with dilute (6%) sulfuric acid and water, and the flask being attached to a filter pump regulated to give gentle suction, 35 ml. of ferric phosphate solution (100 grams of ferric sulfate and 150 ml. of syrupy phosphoric acid and 20 ml. of H_2SO_4 (1 to 1) per liter) are introduced into the suction flask. Just sufficient water then is added to the flask so that when it is connected to the reductor, the end of the reductor tube will dip into the ferric phosphate solution. The reductor should contain a column of 20–30 mesh amalgamated zinc $\frac{3}{4}''$ in diameter and 10″ long. Several solid glass beads are placed at the point of constriction of the tube, followed by layers of glass wool and acid washed asbestos from 2 to 2.5 centimeters, and from 2 to 3 millimeters, respectively, in thickness. Amalgamation of the zinc is effected by treating it with a 2% solution of mercuric chloride for a few minutes and then washing it thoroughly by decantation with water. When idle the reductor should always be kept full to above the top of the zinc with distilled water. The molybdenum solution, which may be at room temperature or slightly warm, is passed through the reductor rapidly. The total time consumed in drawing the molybdenum solution and the wash water through the reductor need not exceed from 1 to 3 minutes. No advantage results from having the solution hot—on the contrary the greater action of the hot acid solution on the zinc is a disadvantage. No increase in accuracy will be secured by use of a slower rate of passage than that specified. When the funnel which forms the inlet of the reductor is nearly but not entirely empty, 150 ml. of cold water are put through in three successive 50 ml. portions, the liquid being drawn down almost to the constriction each time before addition of the next 50 ml. portion. The funnel should never be permitted to become entirely empty and the stopcock should be closed while some of the wash water still remains above the sur-

face of the zinc. By working in this way no air can be drawn through the reductor. The molybdenum solution is green as it passes through the lower part of the reductor, but on coming in contact with the ferric phosphate it is changed to a bright red, due to its immediate partial oxidation, which is of course, accompanied by reduction of a corresponding amount of the ferric salt to the ferrous condition. The solution is immediately transferred to a 500-ml. beaker and titrated with a standard, approximately 0.1 N solution of potassium permanganate until a permanent faint pink color develops. The reactions which occur are shown in part by the following equations:

$$2MoO_3+3Zn+6H_2SO_4=Mo_2(SO_4)_3+3ZnSO_4+6H_2O,$$

$$5Mo_2(SO_4)_3+6KMnO_4+16H_2O=10H_2MoO_4+3K_2SO_4+6MnSO_4+6H_2SO_4$$

or

$$10Mo^{+++}+6MnO_4^-+16H_2O=10MoO_4+6Mn^{++}+32H^+.$$

Working under the conditions described, complete reduction from MoO_3 to Mo_2O_3 is obtained, none of the Mo_2O_3 being reoxidized by the air after passage through the reductor.

Since zinc always contains some iron, a "blank" is run on the two grams used for precipitating the copper, and also on the reductor. This is done by dissolving two grams of the zinc in 75 ml. of 6% sulfuric acid, filtering on an asbestos or alundum filter and putting the solution through the reductor in exactly the same way as the molybdenum solution. The amount of permanganate required to impart a pink tint to the liquid constitutes the "blank" which must be deducted from the burette reading of every analysis.

The number of ml. of permanganate (1 ml. of 0.1 N $KMnO_4$ is equal to .0032 gram Mo), less the "blank," multiplied by 100, and divided by the weight of sample taken, gives the percentage of molybdenum in the ore; the percentage of molybdenum multiplied by 1.5000 gives the molybdenum trioxide.

DETERMINATION OF COPPER

(a) In Molybdenite

Four (4.000) grams of the finely ground sample are treated with 35 ml. of nitric acid (sp.gr. 1.42) and 10 ml. of sulfuric acid (sp.gr. 1.84) in a 250-ml. beaker provided with a clock-glass cover. The solution is digested at a temperature somewhat below the boiling point until most of the molybdenite has dissolved. Subsequently the liquid is boiled until strong fumes of sulfur trioxide are expelled. After having allowed the beaker and its contents to cool, 50 ml. of water are added and the solution is boiled briskly for a few minutes and filtered on a 9-cm. paper into a 250-ml. beaker. The residue is washed thoroughly with hot water and ignited in platinum at a low temperature to burn off the carbon from the filter paper. The precipitate is treated with 10 ml. of HF, 2 ml. of HNO_3 (sp.gr. 1.42) and 1 ml. of H_2SO_4 (sp.gr. 1.84) and the solution evaporated to strong fumes of sulfur trioxide. The contents of the crucible are transferred to the main solution.

A slight excess of a 10% sodium hydroxide solution is added to the filtrate and the solution is boiled for several minutes and filtered on an 11-cm. paper.

The precipitate of ferric hydroxide, etc., is washed with hot water to remove the molybdenum. The precipitate, which will contain all of the copper, is dissolved in 30 ml. of hot dilute (1 : 3) sulfuric acid, the paper being washed thoroughly with hot water and the filtrate and washings being collected in a 150-ml. beaker.

The copper in the solution obtained as above described is completely precipitated in the metallic condition by placing a sheet of pure aluminum (conveniently bent into the form of a triangle 1" in height which stands on its edge in the beaker) in the beaker and boiling for about 10 minutes. Complete precipitation is not obtained until the iron has been reduced, when the aluminum should appear clean and the precipitated copper be detached or only loosely adherent. After removal from the source of heat, the clock glass and sides of the beaker are rinsed with a jet of hydrogen sulfide water. The aluminum, the copper content of which should be accurately determined, is weighed before and after use and a correction is applied for the copper introduced from it.

The solution is filtered on a 9-cm. paper, the copper being transferred to the paper and the aluminum being left as clean as possible in the beaker. The precipitate is washed with H_2S water containing 1% H_2SO_4 and the filtrate and washings are discarded. The copper is dissolved in 5 ml. of hot HNO_3 (1 : 1), this being accomplished by first dropping the acid over the aluminum and then pouring it on the copper. The aluminum and filter paper are both washed with hot water; the filtrate and washings which should not exceed 75 ml. are collected in a 150-ml. beaker. Ten (10) mi. of a solution containing 0.1 gram of $Fe_2(SO_4)_3$ are added and any arsenic and bismuth present are separated by making two ammonia separations. The combined ammoniacal filtrates are boiled down to a volume of about 50 ml. and transferred to a 100-ml. lipless beaker. Two (2) ml. of nitric acid (sp.gr. 1.42) and 2 ml. of H_2SO_4 (sp.gr. 1.84) are added and the copper is determined by electrolysis, a platinum gauze cathode and spiral anode being employed.

If desired, the nitric acid solution of the copper may be collected in a 200-ml. Erlenmeyer flask and the determination completed volumetrically. The solution is evaporated down to a volume of about 2 ml., 25 ml. of water and 5 ml. of bromine water are added and the solution is boiled for several minutes. The purpose of the bromine is to insure the complete oxidation of any arsenic that might be present to its highest state of oxidation. Dilute ammonia (1 : 1) is then added in slight excess and the liquid again boiled until the odor of ammonia is *very faint*. One (1) ml. of glacial acetic acid is added and the boiling is continued for about a minute, when the solution is cooled to room temperature and diluted to 100 ml. with cold water.

The sides of the flask are rinsed down with a jet of cold water, from 5 to 10 ml. of a 30% solution of potassium iodide are added, which results in the reduction and precipitation of the copper and the liberation of a corresponding amount of iodine according to the following reaction:

$$2Cu(C_2H_3O_2)_2+4KI=Cu_2I_2+4KC_2H_3O_2+I_2$$

The liberated iodine is immediately titrated with standard sodium thiosulfate to a slight straw color when several ml. of a freshly prepared 1% starch solution are added and the titration with the thiosulfate solution continued to the

disappearance of the blue color. The reaction takes place according to the following equation:

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

Preparation and Standardization of Solutions

Standard Sodium Thiosulfate—(0.01573 normal) 1 ml. = 0.0010 gram Cu. —Prepared by dissolving 3.90 grams of the pure crystals, $Na_2S_2O_3 \cdot 5H_2O$ in a liter of freshly boiled distilled water. The solution should preferably be allowed to stand several days before being standardized.

Approximately 0.5 gram (exact weight taken) of pure copper is dissolved in 10 ml. of nitric acid (sp.gr. 1.42) and diluted to 500 ml. Twenty-five (25) ml. of this solution are removed with an accurately calibrated pipette, transferred to a 250-ml. Erlenmeyer flask, and the determination completed exactly as described in the above method (paragraphs 3 and 4). The number of ml. of thiosulfate used is divided into the weight of copper taken to give the value per ml. in terms of copper. The value should be 1 ml. = 0.0010 gram Cu.

The thiosulfate solution should be kept in a dark colored bottle. This solution is standardized from time to time, as its strength decreases on standing.

(*b*) In Wulfenite

Four (4.000) grams of the 100-mesh sample are treated with approximately 30 ml. of 10% sodium hydroxide solution in a 250-ml. beaker provided with a clock-glass cover. The solution is boiled briskly for 10 minutes, which is usually sufficient to insure practically complete decomposition of the wulfenite; 150 ml. of hot water are added and the precipitate of iron oxide, etc., which will contain all of the copper, is allowed to settle. The supernatant liquid is decanted through an 11-cm. filter paper and the precipitate is then transferred to the paper and washed well with hot water. The filtrate and washings are discarded. As a result of these operations, separation of the copper from practically all of the molybdenum and from the greater part of the lead is accomplished.

The paper containing the residue is returned to the original 250-ml. beaker and treated with 6 ml. of sulfuric acid (sp.gr. 1.84) and 10 ml. of nitric acid (sp.gr. 1.42). The contents of the beaker are heated cautiously until frothing is nearly over, and then boiled briskly until fumes of sulfuric anhydride are evolved. After having permitted the liquid to partly cool, 10 ml. of nitric acid (sp.gr. 1.42) are added and the evaporation to fumes is repeated. The cover glass and sides of the beaker are rinsed with a few ml. of water and the solution is once more evaporated to fumes in order to insure destruction of all carbonaceous matter from the filter paper and complete expulsion of nitric acid. In practice the total time consumed in making these evaporations is small.

Having allowed the beaker and its contents to cool somewhat, 50 ml. of water are introduced and the solution is boiled for a short while, cooled, and filtered on a 9-cm. paper into a 150-ml. beaker. The precipitate of lead sulfate, etc., is washed with cold 10% sulfuric acid and discarded, the copper passing completely into the filtrate and washings, which should have a total volume of not more than 100 ml.

The copper in the solution obtained as above described, is completely precipitated in the metallic condition by placing a sheet of pure aluminum (conveniently bent into the form of a triangle 1" in height which stands on its edge in the beaker) in the beaker and boiling for about 10 minutes. Complete precipitation is not obtained until the iron has been reduced, when the aluminum should appear clean and the precipitated copper be detached or only loosely adherent. After removal from the source of heat, the clock glass and sides of the beaker are rinsed with a jet of hydrogen sulfide water. The aluminum, the copper content of which must be accurately determined, is weighed before and after use and a correction is applied for the copper introduced into the solution from it.

The determination is completed as described for copper in molybdenite (see paragraphs 4 to 6 inclusive).

DETERMINATION OF PHOSPHORUS

(a) Molybdenite

Four (4.000) grams of the finely ground sample are treated with 35 ml. of nitric acid (sp.gr. 1.42) and 10 ml. of sulfuric acid (sp.gr. 1.84) in a 250-ml. beaker provided with a cover glass. The liquid is heated at a temperature somewhat below the boiling point until decomposition of the mineral appears to have been secured, when it is boiled until strong fumes of sulfuric anhydride are given off. When the residue has cooled somewhat, 40 ml. of water are added and the solution is boiled for several minutes and filtered on a 9-cm. paper into a 300-ml. Erlenmeyer flask. The residue is washed well with hot water, ignited in a porcelain crucible and transferred to a platinum crucible. Two or three drops of sulfuric acid (sp.gr. 1.84), 2 ml. of HNO_3 (sp.gr. 1.42) and several ml. of hydrofluoric acid are added and the solution is evaporated to the complete expulsion of the H_2SO_4. Any small residue remaining is fused at a low temperature with a pinch of potassium pyrosulfate and the melt is dissolved in water and added to the main solution.

A few drops of strong permanganate solution (25 grams per liter) are added to the solution obtained as previously described, and it is boiled to insure complete oxidation of the phosphorus to the tribasic condition. Just sufficient sulfurous acid to decompose the excess permanganate or separated manganese oxide is then added and the boiling is continued for a few minutes longer. A slight excess of ammonia is added and the ferric hydroxide, etc., which will carry down practically all of the phosphorus, is filtered and washed thoroughly with hot water. The precipitate is dissolved in hot dilute nitric acid (sp.gr. 1.135) and the phosphorus is precipitated with "molybdate solution" and determined as described for wulfenite.

(b) Wulfenite

Two (2.000) grams of the agate ground sample of wulfenite are treated with 20 ml. of nitric acid (sp.gr. 1.42) and 10 ml. of sulfuric acid (sp.gr. 1.84) in a 150-ml. beaker. The liquid is heated for a short while at a temperature just below the boiling point and then boiled until fumes of sulfuric anhydride are freely evolved. The residue is taken up with 40 ml. of water, boiled for a few

minutes, cooled, filtered into a 300-ml. Erlenmeyer flask, and the lead sulfate, silica, etc., are washed with cold 5% sulfuric acid. The residue is digested with 50 ml. of ammonium acetate solution (prepared by mixing 16 ml. of NH_4OH (sp.gr. 0.90) with 20 ml. of water and 14 ml. of 99% $C_2H_4O_2$) at a temperature just short of boiling and the solution filtered to remove soluble lead acetate. The filter paper and residue are washed thoroughly with 5% ammonium acetate solution, ignited in a porcelain crucible at a low temperature until the carbon of the filter paper has been burned, and transferred to a platinum crucible. Two (2) ml. of nitric acid (sp.gr. 1.42), 10 ml. of hydrofluoric acid and several drops of sulfuric acid (sp.gr. 1.84) are added and the solution is slowly evaporated to the expulsion of the sulfuric acid. Any remaining residue is fused at a low temperature with a pinch of potassium pyrosulfate, the melt dissolved in water and added to the main solution.

A few drops of strong permanganate solution (25 grams per liter) are added to the filtrate from the lead sulfate and it is boiled to insure complete oxidation of the phosphorus to the tribasic condition. Just sufficient sulfurous acid is added to decompose the excess permanganate or separated manganese oxide, and the boiling is continued for a minute or two longer.

The acid solution is nearly neutralized with ammonia, cooled to 15° C., and to it there are added one gram of tartaric acid, a slight excess of ammonia, 2 grams of pure magnesium sulfate and 4 or 5 glass beads (6 mm. diameter). The solution is chilled thoroughly by immersion in a mixture of crushed ice and salt. The contents of the flask are then shaken *vigorously* (an *efficient* shaking machine can be used to advantage) for about 15 minutes, the solution being chilled several times during the shaking. The glass beads aid in starting the precipitation of the magnesium ammonium phosphate. Fifteen (15) ml. of ammonia (sp.gr. 0.90) are next introduced and the contents of the flask are again chilled thoroughly and shaken briskly for 10 to 15 minutes longer. The flask is then packed in ice in a refrigerator and allowed to stand for 15 hours.

The magnesia precipitate, which may contain small amounts of basic magnesia compounds, iron, and possibly tartrates, is filtered on a 9-cm. paper and washed thoroughly with cold 2.5% ammonia water. The glass beads are transferred to the filter but no attempt is made to remove all of the precipitate from the flask. Under the conditions described, molybdenum, tungsten, and vanadium should all pass completely into the filtrate.

The magnesium ammonium phosphate precipitate is dissolved in 50 ml. of hot nitric acid (1 to 4) and the filter washed well with hot water, the filtrate and washings being caught in the same 300-ml. Erlenmeyer flask. An excess of strong permanganate solution is introduced, the solution boiled for several minutes, cleared by the addition of sufficient sulfurous acid, and further boiled for several minutes. The solution is treated with 6 ml. of ammonium hydroxide (sp.gr. 0.90) and cooled to 25° C. Approximately 0.05 gram of ferrous sulfate (phosphorus-free), 5 grams of ammonium nitrate and 60 ml. of "molybdate solution" are then introduced and the phosphorus is precipitated as ammonium phosphomolybdate by 5 minutes' vigorous shaking. By precipitating the phosphorus with "molybdate solution" at 25° C., any arsenic present will not interfere. This temperature must be strictly adhered to. The precipitate is allowed to settle and the phosphorus is determined by either the alkalimetric

method or the molybdenum reduction method. A " blank " is run on all of the reagents used and deducted.

RAPID DETERMINATION OF MOLYBDENUM IN STEEL[16]

In control work in a steel mill it is essential that laboratory determinations be made quickly and accurately. The following method is a combination of the color method of the U. S. Steel Corporation[17] and that of King.[18] The procedure is rapid and accurate.

Procedure.—Weigh a 0.5-gram sample of steel and place in a 250-ml. beaker. Add 10 ml. of nitric-sulfuric acid mixture. Heat gently until the sample is in solution, then evaporate carefully and rapidly on a hot plate to copious fumes. Do not use a cover glass. Some trouble due to spattering may be experienced at first; however, a little practice in regulating the temperature of the hot plate will readily overcome this difficulty. To obtain concordant results all nitrates must be driven off, which necessitates steady fuming.

Cool the contents of the beaker; add exactly 30 ml. of hydrochloric-sulfuric acid mixture and 30 ml. H_2O and boil until the salts dissolve. The amount of hydrochloric acid used in this operation is very important; too much will cause a fading of the color even before the ether extraction can be made, while not enough of this reagent may present difficulties in the solution of the salts.

Cool the solution to room temperature; add from a buret 5 ml. of potassium thiocyanate solution. Stir well and add 10 ml. of stannous chloride solution from a burette and again stir thoroughly. It is very important that all of the iron be reduced before the extraction is made; therefore, after the addition of the stannous chloride care should be taken that none of the unreduced solution is left on the sides of the beaker.

Extraction with Ether.—Transfer the acid solution to a separatory funnel of suitable size; add 10 ml. of ether and shake well. Return the acid solution to the original beaker and draw off the ether solution into a clean, dry, 50-ml. graduated cylinder. Shake out the acid mixture with successive 10-ml. portions of ether until all color is removed. The volume of ether used for the sample should be approximately the same as is required to give a corresponding color with the standard. Transfer the combined ether solutions to a graduated matching tube.

Color Comparison.—For this operation a Kennicott-Campbell Hurly colorimeter is used in this laboratory. Illumination is supplied by a Wratten Safelight No. 2, made especially for dark-room purposes. This fixture carries a 50-watt bulb, which gives sufficient light and does not materially affect the atmospheric temperature and thus cause a rapid deterioration of the standard due to evaporation of the ether. It is essential that the light be so placed that the illumination is equal on both mirrors.

Place the matching tube containing the unknown in the colorimeter, and adjust the leveling device until the depth of color in the tube containing the

[16] O. L. Maag and C. H. McCollam, The Timken Roller Bearing Co., Canton, Ohio. By courtesy of method appearing in J. Ind. Eng. Chem., 17, 524, 1925.

[17] "Methods of the Chemists of the United States Steel Corporation for the Sampling and Analysis of Alloy Steels," 2nd ed., p. 72, 1921.

[18] J. Ind. Eng. Chem., 15, 350, 1923.

standard equals that of the unknown. Take the reading in milliliters of the standard solution in the graduated matching tube. From this value the molybdenum content of the unknown steel can be calculated.

Standard Solution.—Weight two 0.5-gram samples of standard steel. Run through in the usual manner and make the ether extract up to exactly 50 ml. in the standard matching tube. Place in the colorimeter and compare. If the color tints match, one sample may be diluted to exactly 100 ml. as a standard for low percentage molybdenum, or the two may be united to make a standard for steels with a higher molybdenum content. Transfer to the leveling tube of the colorimeter.

The top of the leveling tube should be covered when not in use, in order to increase the time that a standard can be used. Since the deterioration of a standard is generally due to evaporation of the ether rather than breaking down of the salt, its life is largely dependent on the room temperature. In this laboratory the standard is renewed every 2 hours, two samples of standard steel being kept fuming slightly on the cooler portion of the hot plate, to be used whenever the standard in use is suspected.

Calculation of Results.—If a steel containing 0.23% molybdenum is used as a standard, a 1-gram sample will contain 0.0023 gram of molybdenum; on dilution to 100 ml. each milliliter will contain 0.000023 gram of molybdenum. If 14 ml. of the standard are used to match the color of the unknown steel, the unknown must contain 14×0.000023, or 0.000322 gram. Since the weight of unknown used is 0.5 gram, it will contain twice this amount per gram, or 0.064 %.

$$\frac{\text{Ml. standard (14)} \times \text{grams/ml. (0.000023)}}{\text{Grams sample (0.5)}} = \%\ \text{Mo (0.064)}$$

SOLUTIONS

Nitric-sulfuric acid mixture

H_2O			750 ml.
HNO_3	Sp. gr.	1.42	350 ml.
H_2SO_4	Sp. gr.	1.84	225 ml.

Hydrochloric-sulfuric acid mixture

H_2O			1450 ml.
H_2SO_4	Sp. gr.	1.84	450 ml.
HCl	Sp. gr.	1.19	100 ml.

Potassium thiocyanate solution

KCNS	50 grams
H_2O	1000 ml.

Stannous chloride solution

$SnCl_2$			250 grams
HCl	Sp. gr.	1.19	200 ml.
H_2O			800 ml.

Dissolve the stannous chloride in the hydrochloric acid, boil until clear, and add the water. Add a few pieces of metallic tin to prevent oxidation.

NOTES.—This method has been in use in industrial laboratories for a number of years. The Campbell colorimeter is recommended. Vanadium, nickel, chromium and manganese do not interfere. Copper offers some difficulty which can be eliminated. Annealed high carbon and high chrome steels cannot be handled by this method.

Fading of Red Color of Molybdenum: After Formation by Potassium thiocyanate.—Sometimes this color fades after the ether separation. This is possibly due to the presence of aldehydes from a high alcohol content in the ether. In some cases, however, the coloration fades prior to the ether addition. The authors found in several cases that the solutions were made up in the order given in the method; that is, first the nitric sulfuric acid mixture, then the hydrochloric sulfuric acid mixture, and that the graduate had not been washed between the addition of nitric and the addition of hydrochloric acids to the two different solutions, and the difficulty was apparently due to a trace of nitric acid in the hydrochloric sulfur mixture.

Communicated to the Editor by C. H. McCollam, Chief Chemist, The Timken Steel and Tube Co.

DETERMINATION OF MOLYBDENUM IN ALLOY STEEL

Determination of Molybdenum by Sodium Hydroxide Separation, Lead Molybdate Precipitation (Absence of Tungsten and Vanadium). A. S. T. M. Procedure a.

Solutions. ***Sodium Hydroxide*** (2 N).

Ammonium Acetate (50%).

Lead Acetate (1%).

Dilute Hydrochloric Acid (1 : 4).—200 ml. of HCl (sp.gr. 1.19), 800 ml. of water.

Dilute Hydrochloric Acid (5 : 100).—50 ml. of HCl (sp.gr. 1.19), 1000 ml. of water.

Dissolve 2 g. of the sample in 20 ml. of HCl (sp.gr. 1.19), oxidize with 5 ml. of HNO_3 (sp.gr. 1.42) and expel oxides of nitrogen. Add sodium hydroxide solution (2 N) until the excess of free acid is neutralized, taking care not to produce a red solution (dissolved hydrate) or a precipitate (basic molybdate). Heat the solution to boiling, and run the solution of the steel in rapid drops from a tap funnel into 160 ml. of sodium hydroxide solution (2 N) with constant stirring of the mixture. Dilute the alkaline solution to exactly 500 ml., filter through a dry filter, discard the first few cubic milliliters, and then take exactly 250 ml. of the filtrate. Neutralize the solution with HCl (sp.gr. 1.19), add 5 ml. in excess, boil, add 20 ml. of ammonium acetate solution (50%), and proceed as in the Determination of Molybdenum by Precipitation as Sulfide and Weighing as Lead Molybdate, omitting, however, a second precipitation of the lead molybdate.

Notes.—The above process is of fairly general application. Manganese, nickel, cobalt, aluminum, and the ordinary elements of steel are without influence in the method. Chromium may be partially oxidized to chromate in the alkali treatment but can be reduced to the harmless trivalent condition by adding a few drops of sulfurous acid to the acid solution, prior to the molybdate precipitation. Tungsten and vanadium interfere. Vanadium is not easily removed but the interference of tungsten can be largely overcome by the modification of the method indicated in method (*b*).

(b) Determination of Molybdenum by Sodium Hydroxide Separation, Lead Molybdate Precipitation (Presence of Tungsten and Absence of Vanadium).—Dissolve 2 g. of the sample in a covered beaker in 50 ml. of HCl (sp.gr. 1.19), heat to incipient boiling and digest on a hot-plate at moderate heat. Add a few drops of HNO_3 (sp.gr. 1.42), wait until the vigorous action ceases, and continue to dropwise addition of the acid until the vigorous action ceases. If this is carefully done, no tungstic acid separates at this stage. Next evaporate

the liquid as quickly as possible until tungstic acid begins to separate, and then more slowly until the solution is pasty. Now add 50 ml. of dilute HCl (1 : 4), boil, and set aside for at least 15 minutes. Filter through paper pulp, wash with dilute HCl (5 : 100) and treat the hydrochloric acid solution for molybdenum as above.

DETERMINATION OF MOLYBDENUM. COLORIMETRIC METHOD

(Absence of Tungsten and High Vanadium or Copper)

Solutions. ***Dilute Sulfuric Acid*** (1 : 7).—100 ml. of H_2SO_4 (sp.gr. 1.84), 700 ml. of water.

Dilute Nitric-Sulfuric Acid Mixture.—833 ml. of HNO_3 (sp.gr. 1.20), 167 ml. of H_2SO_4 (1 : 1).

Sulfuric-Hydrochloric Acid Mixture.—450 ml. of H_2SO_4 (1 : 1), 100 ml. of HCl (1 : 1), 450 ml. of water.

Ferric Sulfate.—70 g. of ferric sulfate in a mixture of 120 ml. of HCl (1 : 1), 500 ml. of H_2SO_4 (1 : 1), and 380 ml. of distilled water.

Chromic Sulfate.—Dissolve 50 g. of chromic potassium sulfate in 100 ml. of H_2SO_4 (1 : 1), and 200 ml. of water and heat until the purple color changes to green. Dilute to 1000 ml.

Stannous Chloride.—Dissolve 250 g. of stannous chloride in 200 ml. of HCl (sp.gr. 1.19), and dilute to 1000 ml. with distilled water.

Standard Molybdenum Solution.—Weigh accurately such an amount of a standard ferro-molybdenum (preferably over 50% molybdenum) as will represent exactly 0.5 g. of molybdenum, and transfer the sample to a platinum dish. Add 20 ml. of dilute HNO_3 (1 : 1), and a few milliliters of hydrofluoric acid, warm until the alloy is dissolved and then add 20 ml. of H_2SO_4 (1 : 1) and evaporate until fumes of H_2SO_4 appear. Cool, add 50 ml. of water, boil until all salts are dissolved and then cool and transfer to a liter flask. Add 100 ml. of H_2SO_4 (1 : 1) and dilute the solution to the mark.

Potassium Thiocyanate (5%).—50 g. of KCNS in 1000 ml. of water.

Method.—Transfer 0.5 g. of the steel to a 200 ml. casserole, dissolve in 10 ml. of the nitric-sulfuric mixture, and then evaporate until fumes of H_2SO_4 are evolved. Cool, add 30 ml. of sulfuric-hydrochloric mixture and heat until the salts are in solution. Cool the solution, transfer to a comparison bath and place in a bath for further cooling. To another comparison tube add 25 ml. of the ferric sulfate solution (0.5 g. Fe), 1 ml. of the chromic sulfate solution for each per cent of chromium present, and then 1 ml. of the standard molybdenum solution for each 0.1% of molybdenum expected. Cool both tubes to the same temperature and add to each from a burette 5 ml. of potassium thiocyanate solution (5%). Mix the solution in each tube, add 10 ml. of the stannous chloride solution to each from a burette and well mix each solution for 10 seconds. With dilute H_2SO_4 (1 : 7), dilute the standard to some multiple of its molybdenum content and dilute the test until the colors match. The amounts of molybdenum are then directly proportional to the heights of the columns of liquids.

Notes.—The above method is applicable to steels containing up to 0.5% of molybdenum. Above this percentage the solution of the steel must be divided into aliquot portions and the iron and the hydrochloric acid in the standard varied accordingly.

If the analyst is dealing with steels of approximately the same composition, the iron, chromium (nickel) and molybdenum may be combined so that a single 25-ml. portion is used as the standard.

The amount of hydrochloric acid must be regulated and be the same in the tests as excessive hydrochloric acid causes a fading of the color.

If the steel contains chromium in excess of 1%, difficulty may be encountered in obtaining complete solution after the evaporation to the appearance of fumes of H_2SO_4. In this event, dissolve 0.5 g. of the steel, contained in a 200-ml. flask, in 15 ml. of dilute H_2SO_4 (1 : 1), and 30 ml. of distilled water. When solution is complete, add 15 ml. of $(NH_4)_2S_2O_8$ solution (15%) and boil, add 3 ml. of dilute HCl (1 : 1), boil 10 minutes to expel the excess of persulfate, and to reduce the volume to 30 ml. preliminary to comparison. If any residue remains, add paper pulp, filter, reserve the filtrate, and transfer the paper and pulp to a 150-ml. beaker and add 10 ml. of HNO_3 (sp. gr. 1.42), 5 g. of sodium chlorate and 5 ml. of H_2SO_4 (sp. gr. 1.84). Evaporate to the appearance of copious fumes and repeat the treatment if the solution is not free from color due to organic matter. Cool and add to the reserved filtrate.

RAPID COLORIMETRIC METHOD FOR THE DETERMINATION OF MOLYBDENUM IN CAST IRON AND CHROME CAST IRON [19]

Also applicable to plain Carbon and Alloy Steels.

An accurate colorimetric method for the determination of molybdenum in the presence of chromium, nickel, tungsten, and other elements, is given. It is best adapted to irons containing a maximum of 2% molybdenum. However, good results have been obtained when the molybdenum was as high as 3.40%. The colorimetric method for molybdenum is based on the amber to reddish-brown color developed when the reduced molybdenum is treated with sodium thiocyanate; it is limited to solutions containing not more than 0.05 mg. of molybdenum per ml.

For irons containing 0.25% and under of molybdenum, a 1.000-gram sample is employed; for those containing 0.50 to 1%, a one-half (0.5000) gram sample; and for those containing from 1 to 3%, a one-quarter (0.2500) gram sample. If the sample taken is in the form of drillings it should be further reduced to pass a 40-mesh screen by hammering in a hardened alloy steel mortar. During this crushing frequent screenings should be made in order to keep the sample as near as possible to the desired 40 mesh. If this is done then little, if any, segregation should take place during the weighing of the sample for analysis. The sample is transferred to a 150-ml. covered beaker (containing a glass stirring rod to catch the drip from the cover-glass) and treated with perchloric acid (60%), 5 ml. being used for the one-quarter gram, 10 ml. for the one-half gram and 20 ml. for the 1-gram sample. The contents of the beaker are heated to the boiling point of the acid and the boiling continued until the sample has dissolved and all carbonaceous matter has been destroyed; and, in the case of high-chromium irons until the chromium has been largely converted to chromic acid. Approximately 25 ml. of water are added and the solution is heated to boiling for several minutes to expel free chlorine.

Approximately 2 grams of tartaric acid and a slight excess of 10% sodium hydroxide solution are added in the order mentioned and the solution is heated to about 80° C. for one or two minutes. The liquid is made acid with sulfuric

[19] Method of the Electro Metallurgical Company. Contributed by Mr. T. R. Cunningham.

acid (1 : 1) and then treated with 2 ml. of H_2SO_4 (1 : 1) per each 9 ml. of solution. This will result in a solution containing 10% H_2SO_4 by volume.

In the event it is not convenient to reduce the drillings to 40 mesh a larger sample should be dissolved in hydrochloric acid plus a small amount of nitric acid. Twenty (20) ml. of perchloric acid (60%) are added for each gram of sample taken and the solution evaporated to dense fumes of $HClO_4$. The sides of the beaker are rinsed down with a little water, and in order to expel completely all nitric acid the evaporation to fumes of $HClO_4$ is repeated. The residue is taken up with 50 ml. of water, the solution boiled to expel free chlorine and treated with tartaric acid, 10% NaOH, and H_2SO_4 (1 : 1) as previously described. The solution is cooled to room temperature, transferred to a 200-ml. volumetric flask with 10% H_2SO_4 and made up to the mark with H_2SO_4 of the same strength. The solution is mixed thoroughly and an aliquot portion is taken for the analysis.

The solution having a volume of approximately 50 ml. is cooled to approximately 20° C. and treated with 10 ml. of a 5% solution of sodium thiocyanate and 10 ml. of stannous chloride solution. The liquid is stirred vigorously for several minutes and cooled to room temperature by placing the beaker in a tray of ice water. The stannous chloride reduces the iron to the ferrous condition, the molybdenum from the sexivalent to the quinquevalent, and also any hexavalent chromium not reduced by the tartaric acid, to the trivalent state. The sodium thiocyanate reacts with the reduced molybdenum to form a complex sodium molybdenum thiocyanate, which imparts an amber to reddish-brown color to the solution, depending upon its intensity.

The cooled solution is transferred to a 500-ml. separatory funnel, the beaker rinsed with ether and the rinsings added to the funnel. In the case of small percentages of molybdenum the acid solution is shaken with 50 ml. of ether, and for higher percentages, 100 ml. are used. The acid solution and ether are mixed thoroughly by giving the separatory funnel a vigorous rotary motion and then allowed to stand until the liquid has separated into two distinct layers. The lower or acid layer, which will contain the iron, chromium, nickel, etc., is drawn off into the 150-ml. beaker and the upper layer containing practically all of the molybdenum is then drawn off into a 75-ml. Camp comparison tube if the molybdenum content is 0.25% or under, and into a 200-ml. comparison tube (having an internal diameter of ⅞ in. and length of 24 in.) if higher than 0.25%. (A bend is made in the tube 3 in. from the top to aid in the mixing.) The capacity of the tube is 200 ml. up to the bend. Beginning at 50 ml. and up to 100 ml. the tube is graduated every 10 ml., and from 100 to 200 ml., every 5 ml. The separatory funnel is rinsed with a little ether and the rinsings added to the comparison tube. The lower or acid layer is returned to the separatory funnel and shaken with approximately 25 ml. of ether. The lower layer is drawn off and discarded and should the upper layer have an amber to reddish-brown color it is added to the solution in the comparison tube. After standing for several minutes it is ready for comparison with the standard.

Preparation of Standard for Comparison

With a little practice it is not difficult to estimate approximately the percentage of molybdenum in the sample. Twenty-five ml. of 8% ferric sulfate

solution are transferred to a 150-ml. beaker and treated with 20 ml. of water. The standard molybdenum solution is added from an accurately calibrated burette. The solution is cooled to approximately 20° C. and treated with sodium thiocyanate, stannous chloride, and ether as previously described. It is advisable to allow the molybdenum solution to stand in the comparison tube for several minutes before comparing with the standard, as the intensity of the color sometimes changes at first but remains stable after 7 days and even longer if kept in the dark when not in use.

NOTE.—A standard steel of known Mo content obtained from the Bureau of Standards may be used for the standard.

The percentage of molybdenum in the sample is then determined by comparing the intensity of the color of the ethereal solution of sodium-molybdenum thiocyanate with that of the standard. The darker of the two solutions (the sample and the standard), is diluted carefully with ether and mixed thoroughly until they match exactly. The amount of molybdenum per ml. in the standard is then figured and the calculations of the percentage of molybdenum in the sample is obtained by multiplying the weight of molybdenum in each ml. by the number of ml., dividing by the weight of sample taken, and multiplying by 100. The following example illustrates the calculations involved: In comparing the standard with the sample, 15 ml. of the standard molybdenum solution (1 ml. = 0.0002 gram Mo) were used and diluted to 44 ml. with ether. Therefore,

$$15 \times 0.0002 = 0.0030 \text{ gram Mo}$$

or

$$\frac{0.0030}{44} = 0.000068 \text{ gram Mo per ml.}$$

The sample was diluted to 36 ml., hence,

$$36 \times 0.000068 = 0.00245 \text{ gram Mo in the one-gram sample}$$

or

$$0.245\% \text{ Mo.}$$

Butyl or ethyl acetate may be used in place of the ether. However, when this is done, the darker of the two solutions, the sample, and the standard, must be diluted with butyl or ethyl acetate that has been previously shaken up with sodium thiocyanate and stannous chloride; the lower or aqueous layer of course is drawn off and discarded.

Solutions Required. *Standard Molybdenum Solution.*—One ml. = 0.0002 gram Mo. This solution is prepared by dissolving 0.430 gram of pure sodium molybdate in one liter of water containing 10 ml. of sulfuric acid (1 : 1) and mixing thoroughly. One hundred (100) ml. of this solution are measured carefully by means of an accurately calibrated pipette into a 250-ml. beaker, 12 ml. of sulfuric acid (1 : 1) are added and the solution is put through a Jones Zinc Reductor into 35 ml. of ferric phosphate solution, and titrated with a standard solution of 0.05 N potassium permanganate. (One ml. = 0.0016 gram Mo.)

A blank determination is run on the reductor and the solution of ferric-phosphate (this usually amounts to about 0.3 ml.) by passing 100 ml. of 6%

sulfuric acid and 150 ml. of water (same amount as used in the analysis) through the reductor in exactly the same way as the molybdenum solution, and titrating the liquid with permanganate. The amount of 0.05 N potassium permanganate required to impart a pink tint to the liquid constitutes the blank to be deducted from the burette reading when standardizing the molybdenum solution.

8% Ferric Sulfate Solution.—Eighty grams of ferric sulfate are dissolved in one liter of 20% sulfuric acid. The presence of iron is essential in the preparation of the standard since it has been determined by experiment that the ethereal solution of potassium-molybdenum thiocyanate is more comparable and also more stable than when it is omitted. The iron appears to have a catalytic effect.

Ferric Phosphate Solution.—Twenty-five grams of ferric sulfate are dissolved in 950 ml. of water containing 40 ml. of phosphoric acid (sp.gr. 1.72) and 10 ml. of sulfuric acid (sp.gr. 1.84).

Stannous Chloride Solution.—350 grams of $SnCl_2$ are added to 200 ml. of hydrochloric acid (1 : 1) in a 500-ml. Erlenmeyer flask, the liquid boiled gently until the salt has almost dissolved, transferred to a liter bottle and diluted with freshly boiled water to 1000 ml. A few pieces of metallic tin are introduced to prevent oxidation.

TIME REQUIRED FOR ANALYSIS

Weighing of sample	1/2 minute
Solution of sample, and boiling almost to fumes of sulfur trioxide	8 minutes
Cooling and making ether separation	10 minutes
Comparison with standard	2 minutes

The above time may be reduced after one has become accustomed to the method. It has been found that the intensity of the color remains stable for at least a week, therefore, by making up a sufficient number of fresh standards the beginning of each week, say within a range of .02%, it will only be necessary to dilute the unknown until the colors match. Of course the standards should all be diluted to the same volume. This will aid in reducing the time taken for making the comparison.

Thos. R. Cunningham, Chief Chemist, Union Carbide and Carbon Research Laboratories, Inc., outlined the revision of this chapter and contributed several procedures which are separately acknowledged in the text. We wish to acknowledge a contribution by O. L. Maag and C. H. McCollam, The Timken Roller Bearing Co.

NICKEL [1]

Ni, *at.wt.* 58.69; *sp.gr.* 8.6–8.9; *m.p.* 1452° C.; *oxides*, NiO, Ni_2O_3, Ni_3O_4

Nickel occurs native in meteoric iron and in the minerals josephinite, $FeNi_3$ and awaurite, $FeNi_2$. It occurs in arsenates, antimonates, silicates, sulfides and phosphates, together with cobalt, iron, copper, chromium and zinc.

DETECTION

The H_2S group having been removed in acid solution and iron oxidized to trivalent state, NiS is precipitated with other elements of its group by H_2S passed into its ammoniacal solution. NiS is practically insoluble in cold, dilute HCl (sp.gr. 1.035), effecting its separation (together with CoS) from other elements of the group. The sulfide dissolves on addition of an oxidizing agent such as $KClO_3$ and nickel then is readily identified by the dimethylglyoxime or alpha-benzildioxime test.

Dimethylglyoxime will precipitate nickel as oxime from an acetic acid solution containing sodium acetate and in this manner separate it from cobalt, manganese and zinc. After precipitating iron, aluminum and chromium and filtering them off, the solution is slightly acidified with hydrochloric acid, then is neutralized with sodium hydroxide, and acidified with acetic acid. A solution of dimethylglyoxime is added, when nickel, if present, will be precipitated as a flocculent red precipitate.

Nickel may be detected in the presence of cobalt by adding a solution of sodium hydroxide to the solution of cobalt and nickel until a slight precipitate is formed, then somewhat more potassium cyanide than is necessary to redissolve the precipitate and finally two volumes of bromine water. Warm gently

[1] Nickel was discovered by Cronstedt in 1751 in the mineral niccolite, NiAs. Metallurgists of that day had vainly attempted to extract copper from this mineral, thinking that it contained this element, and in disgust had named it kupfernickel (Old Nick's copper). Cronstedt's effort to solve the difficulty led to his discovery. Nickel is extensively used either as the metal or its alloys. Nickel plated articles, nickel coating on copper or iron, are in daily evidence. In finely divided form it serves as a valuable catalyst in the hydrogenation of oils. The alloys, Monel metal (Ni, Cu, Fe, Mn); German silver, (Cu, Ni, Zn); Nichrome (Ni, Cr); the U. S. nickel coin, are familiar uses of this metal. This type of materials the chemist may be called upon to analyze.

and allow to stand for some time. If a precipitate of nickel hydroxide separates, filter, wash and test with the borax bead.

Nickel may also be detected in the presence of cobalt by precipitating the cobalt as nitrite, as described in the chapter on Cobalt, and then precipitating the nickel as hydroxide with sodium hydroxide and bromine water and testing the precipitate with the borax bead.

Alpha benzildioxime added to an ammoniacal solution of nickel precipitates an intensely red salt having the composition $C_{28}H_{22}N_4O_4Ni$. This precipitate is very voluminous. Silver, magnesium, chromium, manganese and zinc do not interfere with this reaction.

ESTIMATION

The determination of nickel is required, principally, in the analysis of ores, metallic nickel and its alloys, but is also required in the analysis of metallic cobalt and cobalt products as well as in a host of miscellaneous materials.

In the majority of cases the results of a nickel determination are calculated in terms of metallic nickel.

In analytical separations nickel is precipitated with the ammonium sulfide group. Small amounts may pass into the later groups where it separates with calcium and magnesium, if care is not taken in its previous removal.

Nitric acid is the best solvent for ores containing nickel. Details of attack are given in a later section.

PREPARATION AND SOLUTION OF THE SAMPLE

The materials in which nickel occurs ordinarily, may, in general, be brought into solution by treatment with acids, but in the case of some refractory ores and alloys, a fusion is required first to make the acid treatment effective. When treating ores containing sulfides or arsenides a strong oxidizing treatment is necessary to break up these compounds. Metallic nickel may be dissolved easily in nitric acid, more slowly in hydrochloric acid and still more slowly by sulfuric. Nickel alloys may be dissolved in a mixture of hydrochloric acid and nitric acid.

General Procedure for Ores.—One gram of the finely powdered ore is weighed into a porcelain dish and mixed intimately with 3 grams of powdered potassium chlorate. The dish is covered with a watch-glass and 40 ml. concentrated nitric acid added slowly. The dish is allowed to stand in a cool place for a few minutes, then placed on a water bath and digested until the sample is completely decomposed, stirring the mixture frequently with a glass stirring rod,

and adding a little potassium chlorate from time to time until the decomposition is complete. The watch-glass is then removed and any particles that may have spattered on it are washed back into the dish and the evaporation continued to dryness. This evaporation to dryness is repeated with the addition of 10 ml. of concentrated hydrochloric acid, and the silica dehydrated by heating for an hour or more in an air oven at 110° C. The dry residue is moistened with concentrated hydrochloric acid and the sides of the dish washed down with hot water, the mixture heated to boiling and allowed to boil for a few minutes, then withdrawn from the heat and filtered hot, after the insoluble matter has settled.

Treat the filtrate for the removal of interfering elements as directed under Separations.

Fusion Method.

If it is necessary to make a complete analysis it is usually advisable to fuse the sample with a sodium and potassium carbonate mixture containing a little potassium nitrate and then treat in the usual manner to determine silica.

Potassium Bisulfate Fusion.—In the treatment of nickel and cobalt oxides these are ground to a fine powder and a representative sample of 1 gram is fused with 10 grams of potassium bisulfate. This may be done in a porcelain or silica crucible or dish. The melt is extracted with water and the silica filtered off.

Solution of Metallic Nickel and Its Alloys.—From 1 to 5 grams of the well-mixed drillings are treated with a minimum quantity of nitric acid and 20 ml. (1 : 1) sulfuric acid added and the solution evaporated to fumes of sulfur trioxide. Allow the fuming to continue for ten minutes. Dilute carefully with a little water and filter off the insoluble. Continue as directed in the following detailed analyses.

It may be necessary to use a mixture of nitric and hydrochloric acids to bring certain alloys into solution, after which the procedure is the same as above.

SEPARATIONS

Separation of Nickel from Mercury, Lead, Bismuth, Copper, Cadmium, Arsenic, Tin, Antimony, Molybdenum.—The elements are precipitated in acid solution by H_2S as sulfides, nickel remains in solution.

Separation of Nickel from Iron, Aluminum, Chromium, Cobalt, Manganese and Zinc.—Separation of nickel by precipitation as oxime by dimethylglyoxime affords a rapid and quantitative separation. Details of the procedure are given under the Gravimetric Methods.[2]

In the separation from cobalt neutralization of the acid solution by sodium acetate is generally recommended. This procedure also applies to the separation from manganese.

Separation from zinc may be effected by precipitation of nickel oxime in acetic acid solution; or better in Ammoniacal Citrate Solution.

Separation of nickel from zinc may be effected by precipitating ZnS by means of H_2S passed into an 0.01 N sulfuric acid solution or a solution acidified with formic acid. Nickel remains in solution.

Separation of Nickel from Iron.—Two modifications of the oxime method may be used.

[2] L. Tschugaeff, Z. anorg. allgem. Chem., 46, 144, 1905. Ber., 38, 2520, 1905.

(1) The iron, if present as a ferric salt, is converted into a complex salt by adding from 1 to 2 grams of tartaric acid, and the solution diluted to 200 or 300 ml., boiled and the nickel precipitated as the oxime in an ammoniacal solution by the prescribed method. Iron forms no oxime under these conditions.

The iron may be precipitated from this filtrate by colorless ammonium sulfide and the sulfide converted to ferric oxide (Fe_2O_3) by ignition.

(2) Ferric iron is reduced to the ferrous condition by warming with sulfurous acid, in a nearly neutral solution. If the original solution has an excess of acid, it is treated with a solution of sodium hydroxide until a permanent precipitate is formed. This is dissolved with a few drops of hydrochloric acid and the iron reduced by adding from 5 to 10 ml. of a saturated solution of sulfur dioxide or by passing dioxide through the solution. The solution is diluted to 200 or 300 ml. and the solution of dimethylglyoxime added in slight excess, followed by sodium acetate until a permanent precipitate of nickel oxime is formed. After adding 2 grams more of sodium acetate the solution is filtered immediately. The iron is precipitated from the filtrate by oxidizing with bromine water and adding ammonium hydroxide to precipitate the basic acetate of iron.

Procedure (1) is suitable for the determination of nickel in iron and steel.

Cupferron Method.—Small quantities of iron may be precipitated with cupferron in acid solution, the nickel remaining in solution. See chapter on Iron.

Separation of Nickel from Aluminum.—This method is the same as procedure (1) given above.

Separation of Nickel from Chromium.—This separation cannot be carried out in an acetic acid solution. From 1 to 2 grams of tartaric acid are added and from 5 to 10 ml. of a 10% ammonium chloride solution, subsequently. The solution is made ammoniacal, but no precipitate should form. If the solution becomes cloudy, it is acidified with hydrochloric acid and additional ammonium chloride added and again made ammoniacal and the nickel precipitated as oxime according to directions given from this precipitation.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF NICKEL

PRECIPITATION OF NICKEL BY ALPHA BENZILDIOXIME

The alcoholic solution of alpha benzildioxime gives an intensely red precipitate of $C_{28}H_{22}N_4O_4Ni$, when added to ammoniacal solutions containing nickel. The reaction is more characteristic for nickel than is that with dimethylglyoxime and is more delicate. In a volume of 5 ml. (according to F. H. Atack), 1 part of nickel in 2,000,000 parts of water may be detected. In the presence of 100 times as much as cobalt only a faint yellow color is produced

by the cobalt. One part of nickel per million of water will cause precipitation with the compound, whereas no precipitate is formed with dimethylglyoxime under the same conditions. With glyoxime iron produces a pink color, with alpha benzildioxime ferrous salts give a faint violet color, hence do not interfere in the detection of nickel. Silver, magnesium, chromium, manganese, and zinc do not interfere. Since the nickel precipitate with this reagent is exceedingly voluminous it is advisable to have not more than 0.025 gram of nickel in the solution in which the nickel is being determined. The method is adapted to the detection and determination of minute traces of the element, and small amounts up to 10% nickel.

Reagent, Alpha Benzildioxime.—This may be prepared by boiling 10 grams of benzil (not necessarily pure) with 8 to 10 grams of hydroxylamine hydrochloride in methyl alcohol solution. After boiling for three hours the precipitate is filtered off and dried, washed with hot water and then with a small amount of 50% alcohol, and dried. This dried precipitate consists of pure benzildioxime (m.p. 237° C.). A further yield may be obtained by boiling the filtrate with hydroxylamine hydrochloride. The reagent is prepared by dissolving 0.2 gram of the salt per liter of alcohol to which is added ammonium hydroxide to make 5% solution, sp.gr. 0.96 (50 ml. per liter).

Procedure.—A slight excess of the warmed solution of the above reagent is stirred into the ammoniacal solution containing nickel and the whole heated on the water bath for a few moments to coagulate the precipitate. Quantitative precipitation is complete after one minute. The liquid is filtered through a Gooch crucible, with suction, or onto a filter paper, for which a counterpoise has been selected. The counterpoise paper is treated in exactly the same manner as the one containing the precipitate. The precipitate is washed with 50% alcohol, followed by hot water, and is then dried at 110° C. In weighing the precipitate the counterpoise filter is placed in the weight pan of the balance. The precipitate contains 10.93% nickel. Weight of $C_{28}H_{22}N_4O_4Ni \times 0.1093 = Ni$.

NOTES.—Acetone may be used instead of alcohol as a solvent of the reagent. The compound is more soluble in acetone than in alcohol.

The precipitate does not pass through the filter as does the compound with dimethylglyoxime.

The method is affected by the presence of nitrates, hence these must be removed by evaporation of the solution with sulfuric acid to fumes, before the addition of the reagent to the nickel solution.

In the presence of cobalt an excess of the reagent must be used, as in the case of the dimethylglyoxime precipitation.

In the presence of iron and chromium Rochelle salt, sodium citrate or tartaric acid are added to prevent precipitation of the hydroxides of these metals upon making the solution alkaline.

In the presence of manganese a fairly large excess of the reagent is required, the solution being slightly acid with acetic acid.

Zinc and magnesium are kept in solution by addition of ammonium chloride.

Large amounts of copper must be removed by precipitating with hydrogen sulfide before addition of the reagent.

The nickel salt with the reagent forms an extremely voluminous precipitate so that a concentration of 0.09 gram of nickel per 250 ml. is as high as is desirable. The process is applicable to the determination of nickel in the filtrate obtained in the separation of zinc after the removal of the hydrogen sulfide, formic acid, etc.

Method by F. W. Atack, Analyst, 38, 448, 318. Cockburn, Gardiner and Black, Analyst, 38, 439, 443.

PRECIPITATION OF NICKEL BY DIMETHYLGLYOXIME

Preliminary Considerations.—This method has been demonstrated by O. Brunck to be the most accurate and expeditious procedure known for nickel.[3] By this method 1 part of nickel may be detected when mixed with 5000 parts of cobalt or 1 part of nickel may be detected in 400,000 parts of water. The nickel precipitate with this reagent is almost completely insoluble in water and is only very slightly soluble in acetic acid, but is easily decomposed by strongly dissociated acids, so that the precipitation is incomplete in neutral solutions of nickel chloride, sulfate or nitrate. If, however, the free acid formed is neutralized with sodium, potassium or ammonium hydroxides or by addition of the acetate salts of these bases, nickel will be completely precipitated, not even a trace being found in the filtrate.

"The quantitative determination of nickel in the presence of other metals is a simple operation. The nickel should be in the form of a convenient salt.

"The concentration of the solution does not matter; the precipitation can take place either in a solution of the greatest concentration, or in a very dilute solution. The reaction is not hindered by the presence of ammonium salts."

Iron, aluminum, chromium, cobalt, manganese and zinc do not interfere. Theoretically 4 parts of dimethylglyoxime, added as a 1% alcoholic solution, are necessary; a certain excess does no harm provided the alcohol volume does not exceed more than half that of the water solution containing the nickel salt, as alcohol has a solvent action on the oxime. The compound is very stable and volatilizes undecomposed at 250° C.

An excess of ammonium hydroxide is also to be avoided in the solution in which the precipitation takes place.

It has been observed that the precipitate of nickel with dimethylglyoxime may be safely ignited to the oxide NiO without loss, if the filter is first carefully charred without allowing it to take fire, then gradually heated to redness.

Procedure.—Such an amount of the sample should be taken that the nickel be not over 0.1 gram, as glyoxime of nickel is very voluminous and a larger amount would be difficult to filter.[4] If cobalt is present it should not exceed 0.1 gram in the sample taken.[5]

If hydrogen sulfide has been used to precipitate members of the second group, it is expelled by boiling the acid solution and the volume brought to 250 ml.

[3] Z. angew. Chem., 20, 1844 (1907).

[4] Mr. C. Sterling of the International Nickel Co. states that it is their practice to precipitate as much as 0.25 g. or even 0.5 g. of Ni as the glyoxime salt. The precipitate produced in a perchlorate solution containing chromate is comparatively compact, and by dissolving a weighed amount of the reagent in a small volume of hot alcohol the use of large volumes and losses due to solubility of the precipitate in alcohol are avoided. The practical precipitating power of the reagent is 0.25 g. of Ni per g. and a reasonable excess should be allowed. It is therefore possible to use the reagent in the analysis of alloys containing high percentages of Ni.

[5] If the sample contains more than 0.1 gram of cobalt, a large excess of ammonium hydroxide and dimethylglyoxime is necessary to prevent its precipitation, hence it is advisable to take such weights of samples that the cobalt content will be less than this weight. A sample containing 0.03 g. Ni or less is satisfactory—5 ml. of 1% alcoholic glyoxime per 0.01 g. Ni are advisable.

If much copper is present it should be removed.

One or 2 grams of tartaric acid are added to prevent the precipitation of the hydroxides of iron, aluminum and chromium by ammonium hydroxide (this treatment is omitted if these are absent), and 5 to 10 ml. of a 10% solution of ammonium chloride added to keep zinc and manganese in solution, should they be present. Ammonium hydroxide is now added until the solution is slightly alkaline. If a precipitate forms, ammonium chloride is added to clear the solution, followed by ammonium hydroxide to neutralize the acid The solution should remain clear after this treatment, otherwise the ammonium chloride is added in solution or as salt until the solution of the sample will remain clear. It is then heated to nearly boiling and the alcoholic solution of dimethylglyoxime added until the reagent is approximately seven times, by weight, the weight of nickel present. Ammonium hydroxide is now added until the solution has a distinct odor of this reagent. The precipitation of the scarlet red nickel salt is hastened by stirring. It is advisable to place the mixture on the steam bath for fifteen to twenty minutes to allow the reaction to go to completion before filtering. The precipitate is filtered off, into a platinum sponge Gooch crucible, sometimes known as a Neubauer Gooch crucible. (Other forms of Gooch crucible are used for this purpose, but the Neubauer crucible has been found to be most satisfactory.) The precipitate is dried for about two hours at 110 to 120° C. and weighed as $C_8H_{14}N_4O_4Ni$, which contains 20.32% Ni.

Weight of precipitate multiplied by 0.2031 = weight of nickel.

PRECIPITATION OF NICKEL BY ELECTROLYSIS [6]

The solution is freed from members of the H_2S group by precipitation of these in acid solution by H_2S. Zinc is removed by H_2S in a 0.01 N solution preferably of H_2SO_4 or a formic acid solution. Nickel is now deposited by electrolysis.

This deposition is conducted in exactly the same manner as the one described under Cobalt by Electrolysis, and requires that the same precautions be exercised.

In the presence of cobalt the two elements may be determined together by electrolysis as described below and the deposited metal redissolved and nickel determined as oxime. Cobalt is obtained by difference.

Procedure.—After the sample has been brought into solution by one of the methods outlined under Preparation and Solution of the Sample, the solution is evaporated with 20 ml. of 1 : 1 sulfuric acid for every gram of metal in the sample. The evaporation is continued until the solution has fumed strongly for ten minutes. Cool carefully and dilute with 20 ml. of water. Heat the solution to nearly boiling and pass hydrogen sulfide for one hour to precipitate members of the second group. This long treatment is necessary to insure complete precipitation of arsenic. Filter and boil to expel hydrogen sulfide. Add 5 ml. H_2O_2 to insure oxidation of iron compounds to the ferric state and add ammonium hydroxide until just slightly alkaline. Filter off the ferric hydroxide and wash with water containing a small quantity of ammonium hydroxide. To recover occluded nickel dissolve the precipitate in hydrochloric acid and reprecipitate the iron with addition of a little hydrogen peroxide.

[6] W. J. Marsh, J. Phys. Chem., 18, 705 (1914).

Combine the filtrates. Evaporate to about 250 ml. and add 50 ml. of conc. ammonium hydroxide and electrolyze as described under Cobalt.

The increase in weight of the electrode is the weight of cobalt and nickel in the sample. The percentage of cobalt and nickel in the sample is found by multiplying the increase in weight of the electrode by 100 and dividing by the weight of the sample.

NOTE.—The deposition of cobalt and nickel by the above method has been found to be the most accurate of the electrolytic methods. In the solutions containing the organic acids there is always more or less carbide deposited on the cathode with the metal. This causes high results.

NICKEL IN METALLIC NICKEL

This determination may be made in the manner described under Precipitation of Nickel by Electrolysis, separating cobalt before or after the electrolysis or by the method described under Precipitation of Nickel by Dimethylglyoxime. The latter method is recommended.

NICKEL IN COBALT AND COBALT OXIDE

The dimethylglyoxime precipitation is used in combination with the electrolytic precipitation. See chapter on Cobalt.

NICKEL IN NICKEL-PLATING SOLUTIONS

In most cases it is quite unnecessary to separate the cobalt from the nickel in making this determination and, as the principal impurity is usually iron, the best practice is to follow the method given under Precipitation of Cobalt by Electrolysis.

If chlorides or organic matter are present in the solution the preparation of the solution for electrolysis is accomplished in the following manner:

From the well-stirred solution in the plating tank, withdraw about 200 ml. and place in a small beaker. Prepare a 100-ml. burette by thoroughly cleaning it with the sulfuric acid and potassium bichromate mixture and distilled water. Wash finally with a few ml. of the nickel solution and fill the burette with the solution from the plating tank.

Run 66.7 ml. into an evaporating dish and add 2 ml. (1 : 1) sulfuric acid. Evaporate to fumes of sulfur trioxide and allow to fume strongly for ten minutes. Dissolve in a little water. Dilute to 200 ml. carefully, neutralize with a solution of ammonium hydroxide and add 50 ml. of conc. ammonium hydroxide and electrolyze. (See Precipitation of Cobalt by Electrolysis.)

The increase in weight of the cathode in grams multiplied by 2 gives the weight in ounces of nickel in one United States gallon of the plating solution.

VOLUMETRIC DETERMINATION OF NICKEL

DETERMINATION OF NICKEL IN ALLOYS

This method, as described by S. W. Parr and J. M. Lindgren,[7] consists of a modification of the dimethylgloxime method. The precipitation takes place in the usual manner and the precipitate is dissolved in sulfuric acid and the excess titrated with a standard solution of potassium hydroxide.

Procedure.—The alloy is dissolved in nitric or hydrochloric acid and if iron, aluminum or chromium are present twice their weight of tartaric acid is added to prevent their precipitation. If chromium is present ammonium chloride is also added. If manganese or zinc is present hydrochloric acid should be used and most of the free acid evaporated. Add a few ml. of hydrogen peroxide to oxidize any ferrous iron to the ferric state. Dilute to 300 or 400 ml. and neutralize the free acid by sodium acetate. Heat the solution to nearly boiling and add five times as much dimethylglyoxime, in 1% alcoholic solution, as the nickel present. Then completely neutralize with ammonium hydroxide, using a very slight excess (or the solution may be neutralized with sodium acetate). Heat until all the nickel is precipitated. Filter and wash. Place the precipitate and filter in a beaker, add an excess of 0.05 N sulfuric acid, dilute to 200 ml., heat until solution is complete and titrate back with 0.1 N potassium hydroxide solution, taking the first faint yellowish tinge as the end-point. The solutions are standardized against pure nickel.

NOTE.—Cobalt should not exceed 0.1 gram per 100 ml. and an excess of the dimethylglyoxime should be used.

POTASSIUM CYANIDE METHOD FOR NICKEL

The method is rapid and accurate and is especially adapted for determining nickel in steel. Iron, manganese, chromium, vanadium, molybdenum and tungsten do not interfere. Co and Cu should be removed if present. The method depends upon the selective action of potassium cyanide for nickel in preference to silver iodide, used as an indicator, the reactions taking place as indicated, the solution being slightly alkaline with ammonia—

(a) $Ni(NH_3)_6SO_4+4KCN=K_2Ni(CN)_4+K_2SO_4+6NH_3$ (N.B. $4KCN \approx Ni$)

When the double cyanide of nickel has formed, KCN reacts with AgI.

(b) $AgI+2KCN=KAg(CN)_2+KI$ (N.B. $2KCN \approx Ag$)

Reagents.

N/10 Silver Nitrate.—10.788 grams of pure silver are dissolved in nitric acid and made to 1000 ml. or 16.99 g. of the silver nitrate salt. (See Index for reagent.) One ml. $\approx$0.01302 g. KCN.

If preferred the reagent may be made to be equivalent to about 0.001 gram Ni per ml. by dissolving 5.85 grams of $AgNO_3$ per liter.

Potassium Iodide.—25% solution.

[7] S. W. Parr and J. M. Lindgren, Trans. Am. Brass Founders' Assoc., 5, 120 (1912).

N/10 Potassium Cyanide.—13.5 grams of pure KCN are dissolved in water, 5 grams of KOH added and the solution made to 1000 ml.

The cyanide solution is standardized against the silver nitrate solution.

If it is desired to have a solution equivalent to 0.001 g. Ni, 5 grams of KCN per liter is the approximate strength required.

Standardization of the Cyanide.—Fifty ml. of the KCN solution are diluted to about 150 ml., 5 ml. of the KI reagent added and the solution titrated with the standard $AgNO_3$ reagent until a faint permanent opalescence is obtained. A drop of the KCN solution should be sufficient to clear this. Note the number of ml. required and calculate the normality factor of the cyanide in terms of the silver nitrate reagent.

Example.—Suppose 49 ml. of the silver nitrate reagent were required for the 50 ml. of the cyanide solution, then the normality would be $49 \div 50 \times N/10$ or 0.98 N/10.

One ml. N/10 solution is equivalent to 0.002934 gram nickel.

The reagent may be standardized against a nickel steel of the U. S. Bureau of Standards, following the procedure given below and calculating as follows:

$$\text{Nickel factor} = \frac{\text{Gram Ni in standard taken}}{(\text{ml. KCN required}) - (\text{ml. KCN equivalent to 5 ml. } AgNO_3)}$$

Citric Solution.—Two hundred grams of $(NH_4)_2SO_4$, 150 ml. concentrated NH_4OH and 120 grams of citric acid per 1000 ml.

Procedure.—One gram of the steel drillings or such an amount of material as contains not over 0.1 g. Ni, is dissolved in a beaker with 20 ml. of hydrochloric acid (1 : 1). When action ceases 10 ml. of nitric acid (1 : 1) are added and the solution boiled until the red nitrous acid fumes are driven off.

About 100 ml. of the citrate solution are added. If 2% or more of chromium is present the amount of citrate solution is doubled. The solution is now diluted to about 250 ml.

Exactly 5 ml. of the standard silver nitrate solution are now added from a pipette or burette, and then ammonium hydroxide, drop by drop, until the cloudiness caused by the silver chloride just disappears. Two ml. of the potassium iodide solution are now added.

The solution is titrated with the standard potassium cyanide solution with constant stirring until the turbidity just disappears. The end point is reached when there is no longer a distinction in clearness of the drop of the reagent and its surrounding liquid to which it is added.

If the end-point is passed, a measured amount of silver nitrate (5–10 ml.) is added and the cyanide titration repeated.

Calculation.—Deduct the ml. KCN equivalent of the total silver nitrate solution used from the total ml. of the KCN solution required in the titration. The remainder is the potassium cyanide required by the nickel.

The ml. KCN required by Ni multiplied by the factor for Ni = gram nickel in the sample.

1. A large excess of ammonia is to be avoided as the AgI is soluble in a large excess.

2. The presence of sulfates increases the sensibility of the end-point.

3. The silver nitrate solution should not be stronger than that indicated in the method as there is danger of the iodide of silver settling out as a curdy precipitate in stronger solutions.

4. A white film is apt to form on the surface of the liquid if exposed to the air for some time. This produces no error.

CYANIDE TITRATION METHOD

(Routine)

A. S. T. M. Method for Steel

I. Preliminary Treatment

(a) Preliminary Separation with Dimethylglyoxime. (Presence of Chromium, Copper, Cobalt and Small Amounts of Tungsten).—Proceed as in the gravimetric method until the dimethylglyoxime precipitate has been dissolved in aqua regia, and then evaporate the solution to 50 ml. or until free from dimethylglyoxime and oxidizing gases. Cool the solution, with ice if desired, neutralize with NH_4OH (sp. gr. 0.90) (rosolic acid is a convenient indicator), add 5 ml. in excess, dilute to 250 ml., and proceed as in the final titration below.

(b) Preliminary Ether Extraction (Absence of Cobalt and More than 1% Tungsten).

Solutions. *Dilute Hydrochloric Acid* (3 : 2).—600 ml. HCl (1.19 sp. gr.) and 400 ml. H_2O.

Acidulated Hydrogen Sulfide Water.—Add 25 ml. of HCl (sp. gr. 1.19) to 600 ml. of distilled water and saturate with H_2S.

Method.—In a 150 ml. beaker dissolve 1 g. of the steel in 20 ml. of the dilute HCl (3 : 2), add about 2 ml. of HNO_3 (sp. gr. 1.42) to oxidize the iron, and boil to expel the oxides of nitrogen. Cool, and transfer the solution into an 8-oz. separatory funnel, rinsing the beaker with small portions of the dilute HCl (3 : 2). Add 50 ml. of ether, shake for 5 minutes, let settle for 1 minute, and then draw off the lower clear solution into another 8-oz. separatory funnel. Add 10 ml. of dilute HCl (3 : 2) to the solution in the first separatory funnel, cool, shake thoroughly, allow to settle for 1 minute, and then draw off the lower clear solution into the second separatory funnel. To the combined solutions in the second separatory funnel add 50 ml. of ether, shake for 5 minutes, let settle for 1 minute, and then draw off the clear layer into a 150-ml. beaker. Heat the aqueous solution gently to expel the ether, add 0.2 g. of potassium chlorate, boil until the chlorate is decomposed, dilute to 100 ml. with hot water, make faintly ammoniacal, and boil for 5 minutes. Filter and wash with hot water. To the filtrate add 10 ml. of HCl (sp. gr. 1.19), heat just short of boiling and precipitate the copper with hydrogen sulfide. Filter and wash with acidulated hydrogen sulfide water. Boil the filtrate to expel hydrogen sulfide, neutralize with ammonia as in (*a*), add 5 ml. in excess, dilute to 250 ml. and proceed as in the final titration below.

(c) Direct Titration (Absence of Copper, Cobalt, and More than 1% Tungsten).

Solutions. *Dilute Nitric Acid* (sp. gr. 1.20).—380 ml. of HNO_3 (sp. gr. 1.42) 620 ml. of water.

Ammonium Persulfate (15%).—Make up as needed by dissolving 15 g. of the salt in 100 ml. of distilled water.

Dilute Ammonia (1 : 1).—Equal volumes of NH_4OH (sp. gr. 0.90) and water.

Sulfuric-Citric Acids.—Dissolve 200 g. of citric acid in a cooled mixture of 100 ml. H_2SO_4 (sp. gr. 1.84) and 900 ml. of distilled water.

Method.—Transfer 1 g. of the sample to a 400-ml. beaker, treat with 20 ml. of dilute HNO_3 (sp. gr. 1.20) and heat until the sample is dissolved. Add 8 to 10 ml. of ammonium persulfate solution (15%) and continue the boiling for five minutes. Cool the solution, add 50 ml. of the sulfuric-citric acid mixture, and then dilute HN_4OH (1 : 1) until the solution is just alkaline to litmus, when an excess of 5 ml. is added. In case a precipitate is formed, use more citric acid. The neutralization of the solution should be made as soon as possible after the addition of the citric acid, as otherwise this may reduce traces of iron. Cool to room temperature, dilute to 250 ml. and proceed as in the final titration below.

If chromium is present in amounts over 1%, dissolve the steel in 20 ml. of dilute H_2SO_4 (1 : 4), oxidize with 5 ml. of HNO_3 (sp. gr. 1.42), boil 5 minutes, cool, add 50 ml. of sulfuric-citric acid mixture and proceed as above.

II. Final Titration

Solutions. ***Potassium Iodide*** (10%).—Ten g. of KI in 100 ml. of water.

Standard Silver Nitrate.—Dissolve 5.7903 g. of $AgNO_3$ in distilled water and dilute to exactly 1000 ml.

Standard Potassium Cyanide.—Dissolve 4.5 g. of KCN in 1000 ml. of distilled water containing 1 g. of KOH. Standardize this solution against the standard silver nitrate solution as follows: To a 400-ml. beaker add 100 ml. of water, 3 ml. of HN_4OH, 2 ml. of potassium iodide solution (10%), and finally 30 ml. of silver nitrate solution from a burette. Titrate with the cyanide solution until the solution is perfectly clear, and then add more silver nitrate solution until a faint cloudiness is obtained which can be dispelled by two drops of the cyanide solution. Adjust the cyanide solution so that it is equivalent to the silver nitrate solution and check the theoretical value (0.001 g. nickel) by standardizing, by the procedure chosen, against a steel of known nickel content as determined by the gravimetric dimethylglyoxime method.

Method.—Add 2 ml. of potassium iodide solution (10%) to the solution prepared as in (*a*), (*b*), or (*c*) and then from a burette add 3 ml. of standard silver nitrate solution. Slowly add standard cyanide solution, with constant stirring, until the solution is perfectly clear. Continue the addition of the silver nitrate solution and titration with cyanide solution until the cloudiness of the solution, due to the addition of two drops of the standard silver nitrate, is just expelled by the final addition of two drops of the standard cyanide. Each cubic centimeter excess of standard cyanide solution required over standard silver nitrate solution used in the titration represents 0.1% of nickel.

If cobalt is present, an unsatisfactory end-point will be obtained if the titration is carried out as directed after a preliminary separation by methods (*b*) or (*c*). Cobalt may, however, be titrated satisfactorily provided it is first oxidized to the trivalent condition by boiling the ammoniacal solution with $NaClO_3$ prior to the titration with cyanide. In this case, the compound $K_2Co(CN)_6$ is formed and the titration represents the combined effect of nickel and cobalt. (See the Determination of Cobalt in Tungsten Steel by the Cyanide Titration Method (Routine).)

THE ANALYSIS OF METALLIC NICKEL[8]

Discussion.—Nitric acid is the general solvent for nickel. The strength of the acid may be varied in accordance with the determination in view: concentrated acid is used for gravimetric sulfur; 1 : 4 acid facilitates the determination of manganese in high silicon material; and 1 : 9 acid may be used for residue analyses.

Solution of the sample in dilute HBr saturated with Br_2 followed by evaporation to dryness and baking will remove As, Sb, and Sn.[9] The bromide residue is decomposed by HNO_3, fumed with H_2SO_4 or $HClO_4$, and the usual procedures are followed.

[8] Outline prepared by Mr. C. Sterling, Research Chemist, International Nickel Co.

[9] Anonymous, Chemistry and Industry, 53, 615 (1934).

Silicon may be removed by dehydration with HCl, H_2SO_4, or $HClO_4$ followed by filtration. Addition of HF to the HNO_3 solution followed by evaporation with H_2SO_4 is useful in many cases. The operation may be carried out in glass if elements introduced by corrosion of the reaction vessel do not interfere in subsequent operations and determinations.

Most of the elements found in very small amounts may be gathered by precipitation with NH_4OH. Ferric ion may be added to the solution if necessary. In general, the techniques developed for the analysis of refined copper are applicable. The use of MnO_2 in dilute acid solution would probably apply, although the presence of Co should not be overlooked.[10, 11]

The ammonia precipitate will contain all the Fe, Al, Ti, Zr, Ta, Cb and Sn, and, if conditions are properly regulated, all of small quantities of P, As, Sb, Bi, Se, Te, Pb, Cr, V, and W. Manganese divides, but may be retained in the precipitate by the addition of an oxidizing agent. Ca and Mg will be found in the filtrate containing the bulk of the Cu and Ni; they may be precipitated together from this solution as phosphates and subsequently separated and purified.[12]

Precipitation by NH_4OH in the presence of perchlorates must be done in a large volume of hot solution with only a slight excess of reagent. $Ni(NH_3)_6(ClO_4)_2$ crystallizes readily and will contaminate the precipitate if proper precautions are not observed. It is interesting to note that Ni and Co may be nearly quantitatively precipitated in cold, strongly ammoniacal perchlorate solutions. Tartrate does not interfere. Co is readily oxidized to a soluble form even by exposure to air.

Cyanide solutions offer possibilities for a number of separations. Fe and Al may be sharply separated from Ni by NH_4OH in the presence of the complex cyanide.[13, 14] Evans precipitates ZnS in a buffered cyanide solution,[15] and it seems probable that some useful separations by 8-hydroxyquinoline could be made in this medium.[16] Extraction by dithizone will probably be of service when optimum conditions have become established.

Procedures.—The routine analysis of metallic nickel involves determinations of C, Si, S, Cu, Mn and Fe. Nickel (plus cobalt) is found by difference. Direct determinations of Ni+Co+Cu by electrolysis from ammoniacal sulfate solutions give high values and the deposit will contain Mn if it is present.

Carbon.—Carbon is determined on 3 gram samples by direct combustion in the usual type of train used for steel analysis. A temperature of 1200° C. is advisable and the period of burning should be at least 20 minutes. Ingot iron may be used as a flux to decrease the time needed for the combustion.

Silicon and Sulfur.—These determinations are conveniently combined on 10 gram samples. The sample is mixed with 1 gm. of $KClO_3$ and dissolved with HNO_3. The HNO_3 is removed by two evaporations to dryness with HCl. The chlorides are moistened with 2–3 ml. of HCl, dissolved in water, and the silica is filtered off and determined. Sulfur is precipitated in the filtrate with $BaCl_2$ solution and is determined as usual after standing 18–24 hours.

[10] Park and Lewis, Ind. Eng. Chem., Anal. Ed. 5, 182 (1933).
[11] Park, Ind. Eng. Chem., Anal. Ed. 6, 189 (1934).
[12] Hillebrand and Lundell, "Applied Inorganic Analysis," p. 488.
[13] Lundell, Hoffman and Bright, "Chemical Analysis of Iron and Steel," p. 278.
[14] Chirnside, Analyst, 59, 278 (1934).
[15] Evans, Analyst, 60, 464 (1935).
[16] T. Heczko, Chem. Ztg., 58, 1032 (1934); Analyst, 60, 120 (1935), abstract.

Sulfur may be determined by the evolution method. The fine drillings or sawings are dissolved by conc. HCl in an all glass evolution flask equipped with a water-cooled reflux condenser. The evolved gases are passed through a gas washing bottle containing water before entering the absorption medium.

Silicon in high silicon nickel should be determined on 1 gram samples after dehydration with 15 ml. of 70% $HClO_4$.

Copper.—Copper in ordinary amounts is determined by direct electrolysis. When it is very low it is best to concentrate it by double precipitation with H_2S and determine it colorimetrically. To determine Cu by direct electrolysis 5 grams of sample are dissolved in HNO_3. The excess of acid is removed by evaporation to a syrup. After dilution, NH_4OH is added until a precipitate forms and is followed by 10–15 ml. of 1 : 1 H_2SO_4. The solution is diluted to 250 ml. to prevent crystallization and electrolyzed for Cu.

Manganese.—Routine determinations of Mn are made by the bismuthate method applied directly to HNO_3 solutions of 1 gram samples. A correction must be applied to the titration to compensate for the excess $KMnO_4$ used to overcome the color of the nickel nitrate.

Umpire determinations are made by the bismuthate method after precipitating the Mn from HNO_3 solutions of 5 gram samples by means of NH_4OH and $(NH_4)_2S_2O_8$. A fairly large excess of HN_4OH is necessary to secure a good separation of Co.

Iron.—Iron is gathered from HNO_3 solutions of 5 gram samples by double precipitation with NH_4OH. The ammonia precipitate is dissolved in HCl, the Fe is reduced with $SnCl_2$ and titrated with dilute $K_2Cr_2O_7$, using diphenylamine as an internal indicator.

Aluminum.—Aluminum may be concentrated by precipitation with NH_4OH and freed from most impurities by electrolysis in a Hg cathode cell. The method of determination depends on the amount of Al and elements associated with it. Provision should be made for Si, Mn, and P; also such elements as Ti, V, Zr, Be, U, and Ce. The ammonia, phosphate, quinolate, or colorimetric methods have been used.[17]

Nickel.—Dissolve 0.3 gm. of drillings in an 800 ml. beaker with HNO_3. Add 15 ml. of 70% $HClO_4$ and evaporate cautiously to fumes. HF may be added to high silicon material. Boil gently for 10–15 minutes. Cool and add 400 ml. of water. Add 10 ml. of 25% ammonium citrate solution. Neutralize with NH_4OH and add 1–2 ml. excess. Dilute to 500 ml. and heat to 90° C. Precipitate the nickel with 1.5 gm. of dimethylglyoxime dissolved in 40 ml. of hot alcohol. Stir vigorously and allow to stand for ½–1 hour.

Filter the nickel dimethylglyoxime on a 15 cm. paper and wash with hot water. Transfer the precipitate to a 600 ml. beaker and dissolve it with 15 ml. of HNO_3 and 15 ml. of HCl. Add 20 ml. of 1 : 1 H_2SO_4 and evaporate to fumes. Add HNO_3 dropwise to the fuming residue until all organic matter is destroyed. Continue fuming until nitric acid is removed. Cool, dissolve salts in 100 ml. of water. Neutralize with NH_4OH and add 25 ml. excess. Dilute to 200 ml. and determine Ni by electrolysis.

This method is satisfactory for all ordinary purposes. For work of the highest accuracy it is recommended that the nickel dimethylglyoxime be reprecipitated with the usual dilute reagent, filtered on fritted glass, dried, and

[17] Peters, Chemist-Analyst, 24, No. 4 (1935).

weighed. The combined filtrates should be concentrated, the organic matter destroyed, and the residual nickel recovered.

Cobalt.—The volumetric method of Sarver [18] may be applied to a solution of the crude cobalt obtained by direct precipitation with nitroso beta napthol. The usual small amounts of Fe and Cu present do not interfere. Volumetric methods based on oxidation of Co in ammoniacal citrate solution by means of potassium ferricyanide will probably prove to be satisfactory.[19, 20]

The following method is suitable for occasional accurate determinations:

Dissolve 3 grams of drillings in 25 ml. of nitric acid and evaporate the solution to a syrup. Add 50 ml. of hydrochloric acid and evaporate to dryness. Again add 50 ml. of hydrochloric acid and evaporate to dryness. Drench the residue with 10 ml. of hydrochloric acid and dilute to 100 ml. with warm water. Heat until salts are in solution, filter and wash with hot water.

Ignite the paper and contents in a platinum crucible, cool and add 1 drop of 1 : 1 sulfuric acid and a little hydrofluoric acid. Evaporate until fumes of sulfuric acid are given off, then fuse the residue with a pinch of sodium bisulfate. Dissolve the melt in water and add to the reserved filtrate.

Dilute the solution to 200 ml., heat to boiling, and pass a rapid stream of hydrogen sulfide for 30 minutes. Allow the sulfides to settle for 1 hour, filter and wash with 1 : 99 hydrochloric acid saturated with hydrogen sulfide. Discard the precipitate and boil the hydrogen sulfide off from the filtrate. Oxidize with a pinch of ammonium persulfate and evaporate to 100 ml.

Neutralize the solution with ammonia and add 20 ml. excess of hydrochloric acid. Dilute to 200 ml., cool to 10° C., and add an excess of cool 6% cupferron solution. Filter and wash with cold 5 : 95 hydrochloric acid. Discard the precipitate and dilute the filtrate and washings to 400 ml.

Add one and one-half times as much nitroso beta napthol as is required to precipitate the cobalt. (1 gm. of the reagent dissolved in 15 ml. of glacial acetic acid and filtered. 15 ml. precipitate approximately .06 grams of cobalt.) Heat to 60°–70° C. by digesting on steam bath for 20 minutes and allow to stand for several hours.

Filter and wash with hot 1 : 3 hydrochloric acid and then with hot water. Ignite in a porcelain crucible. Transfer the oxides to a beaker, dissolve in hydrochloric acid and evaporate to dryness. Add 15 ml. of hydrochloric acid, dilute to 300 ml., and heat to 90° C. Precipitate the cobalt with nitroso beta napthol, let stand several hours, filter and wash as before. Ignite to constant weight at 750°–850° C. and weight as Co_3O_4.

The weighed oxide should be corrected by a blank carried through all steps in the determination, or it may be dissolved in hydrochloric acid and any impurities found deducted. (Mainly iron from the reagent.)

Dr. W. L. Savell contributed a portion of the original draft of this chapter. Methods of the International Nickel Company were contributed through the courtesy of Mr. Thomas Fudge, and revised by Mr. C. Sterling, research chemist of the company.

[18] Sarver, Ind. Eng. Chem., Anal. Ed. 5, 275 (1933).

[19] Dickens and Maassen, Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf, 17, 191 (1935).

[20] Tomicek and Freiberger, J. Am. Chem. Soc., 57, 801 (1935).

NITROGEN

Element. N_2, *at.wt.* 14.008; D. (*air*) 0.9674; *m.p.* −210°; *b.p* −.195.8° C.; *oxides*, N_2O, N_2O_2, N_2O_3, N_2O_4, N_2O_5.

Ammonia. NH_3, *m.w.* 17.03; D. (*air*) 0.5971; *sp.gr. liquid* 0.6234; *m.p.* −77.7°; *b.p.* −33.5° C. *Crit. temp.* 130°; *liquid at* 0° *with* 4.2 *atmospheres pressure. Commercial* 28% NH_3, *sp.gr.* 0.90.

Nitric Acid. HNO_3, *m.w.* 63.02; *sp.gr.* 1.50; *m.p.* −43.2; *b.p.* 86° C. *Boiling-point of commercial* 95% *acid is a little above* 86°, *but gradually rises to* 126° *and the strength of acid falls to* 68.9%, *sp.gr. is then* 1.42. *The acid now remains constant, the distillate being of the same strength.*

Nitrogen[1] occurs free in air to extent of 78%+ by volume and 76%− by weight.

Air weight of 1 liter = 1.293 grams. With oxygen as 32, air = 28.95.

COMPOSITION OF AIR. ON THE BASIS OF 1000 LITERS OF ATMOSPHERE

Element	Liters per 1000 l.	Weight per 1000 l. grams	Per cent by Vol.	Per cent by Wt.
Nitrogen	780.3	975.80	78.1	75.47−
Oxygen	209.9	299.84	21.0	23.19−
Argon	9.4	16.76	0.9	1.296+
Carbon dioxide	0.3	0.59	0.04	0.045
Hydrogen	0.1	0.01		
Neon	0.015	0.01339		
Helium	0.0015	0.00027		
Krypton	0.00005	0.00018		
Xenon	0.000006	0.00003		

Nitrogen is found combined in nature as potassium nitrate (saltpeter), KNO_3; sodium nitrate (Chili saltpeter), $NaNO_3$, and to a less extent as calcium nitrate $Ca(NO_3)_2$. It occurs in plants and in animals, in the proteid substances, blood, muscle, nerve substance, in fossil plants (coal), in guano, ammonia and ammonium salts.

Free nitrogen is estimated in the complete analysis of gas mixtures. In illuminating gas the other constituents are removed by combustion and absorption and the residual gas measured as nitrogen.

Total nitrogen in organic substances is best determined by decomposition of the materials with sulfuric acid as described later, and estimating the nitrogen from the ammonia formed.

Combined nitrogen in the form of ammonia and nitric acid specially concerns the analyst. In the evaluation of fertilizers, feedstuffs, hay, fodders, grain, etc., the nitrogen is estimated after conversion to ammonia. Ammonia, nitrates and nitrites may be required in an analysis of sewages, water, and soils. Nitric acid is determined in Chili saltpeter, in the evaluation of this material for

[1] Nitrogen was established as an element by Lavoisier who named the gas azote (lifeless), the name by which nitrogen is known in France.

the manufacture of nitric acid or a fertilizer, the nitrate being reduced to ammonia and thus estimated.

The determination of nitrogen is required in tests of a large number of compounds containing nitrogen in combination, such as the azo compounds, antipyrine, amides, imides, brucine, hydrazine, cyanide, phenylhydrazine, isatin, atrophine, caffeine, strychnine, nicotine, cinchonidine, cocain etc.

DETECTION

Element. Organic Nitrogen.—Organic matter is decomposed by heating in a Kjeldahl flask with concentrated sulfuric acid as described under Preparation and Solution of the Sample. Ammonia may now be liberated from the sulfate and so detected.

Nitrogen in Gas.—Recognized by its inertness towards the reagents used in gas analysis. The element may be recognized by means of the spectroscope.

Ammonia.—Free ammonia is readily recognized by its characteristic odor. A glass rod dipped in *hydrochloric acid* and held in fumes of ammonia produces a white cloud of ammonium chloride, NH_4Cl.

Moist red litmus paper is turned blue by ammonia. Upon heating the paper the red color is restored, upon volatilization of ammonia (distinction from fixed alkalies).

Nessler's Test.[2]—Nessler's reagent added to a solution containing ammonia, combined or free, produces a brown precipitate, $NHg_2I \cdot H_2O$. If the ammoniacal solution is sufficiently dilute a yellow or reddish-brown color is produced, according to the amount of ammonia present. The reaction is used in determining ammonia in water.

Salts of ammonia are decomposed by heating their solutions with a strong base such as the hydroxides of the fixed alkalies or the alkaline earths. The odor of ammonia may now be detected.

Nitric Acid. ***Ferrous Sulfate Test.***—About 1 to 2 ml. of the concentrated solution of the substance is added to 15 to 20 ml. of conc. sulfuric acid in a test-tube. After cooling the mixture, the test-tube is inclined and an equal volume of a saturated solution of ferrous sulfate is allowed to flow slowly down over the surface of the acid. The tube is now held upright and gently tapped. In the presence of nitric acid a brown ring forms at the junction of the two solutions.

The test for nitrate may be made according to the quantitative procedure given for determining nitric acid (see later). It should be remembered that

[2] The reagent is made by dissolving 20 grams of potassium iodide in 50 ml. of water, adding 32 grams of mercuric iodide and diluting to 200 ml. To this is added a solution of potassium hydroxide—134 grams KOH per 260 ml. H_2O.

ferrous sulfate should be present in excess, otherwise the brown color is destroyed by the free nitric acid. Traces of nitric acid in sulfuric produce a pink color with the sulfuric acid solution of ferrous sulfate. (See Determination of Nitric Acid—Ferrous Sulfate Method.)

Ferro- and ferricyanides, chlorates, bromides and bromates, iodides and iodates, chromates and permanganates interfere.

Diphenylamine Tests for Nitrates.—$(C_6H_5)_2NH$ dissolved in sulfuric acid is added to 2 or 3 ml. of the substance in solution on a watch-glass. Upon gently warming a blue color is produced in presence of nitrates. Nitric acid in sulfuric acid is detected by placing a crystal of diphenylamine in 3 or 4 ml. of the acid and gently warming. Cl', Cl^v, Br^v, I^v, Mn^{vii}, Cr^{vi}, Se^{iv}, Fe^{iii} and other oxidizing agents interfere.

Copper placed in a solution containing nitric acid liberates brown fumes.

Phenolsulphonic Acid Test.—See chapter on Water Analysis.

Detection of Nitrous Acid. *Acetic Acid Test.*—Acetic acid added to a nitrite in a test-tube (inclined as directed in the nitric acid test with ferrous sulfate), produces a brown ring. Nitrates do not give this. If potassium iodide is present in the solution, free iodine is liberated. The free iodine is absorbed by chloroform, carbon tetrachloride or disulfide, these reagents being colored pink. Starch solution is colored blue.

Nitrous acid reduces iodic acid to iodine. The iodine is then detected with starch, or by carbon disulfide, or carbon tetrachloride.

Potassium Permanganate Test.—A solution of the reagent acidified with sulfuric acid is decolorized by nitrous acid or nitrite. The test serves to detect nitrous acid in nitric acid. Other reducing substances must be absent.

ESTIMATION

We will take up a few of the characteristic substances in which nitrogen estimations are required, e.g., in organic substances as proteids, in soils and fertilizers; in ammonium salts, nitrates, and nitrites, free ammonia in ammoniacal liquors, nitric acid in the evaluation of the commercial acid and in mixed acids.

In general nitrogen is more accurately and easily measured as ammonia, to which form it is converted by reduction methods. Large amounts are determined by titration, whereas small amounts are estimated colorimetrically. Nitric acid and nitrates may be determined by direct titration by the Ferrous Sulfate Method outlined later. The procedure is of value in estimation of nitrates in mixed acids. The nitrometer method for determining nitrates

(including nitrites), and the free acid in mixed acids, is generally used by manufacturers of explosives.

PREPARATION OF THE SAMPLE

It will be recalled that compounds of ammonia and of nitric acid are generally soluble in water. All nitrogen compounds, however, are not included. Among those which are not readily soluble the following deserve mention: compounds of nitrogen in many organic substances; nitrogen bromophosphide, $NPBr_2$; nitrogen selenide, NSe; nitrogen sulfide, N_4S_4; nitrogen pentasulfide N_2S_5; ammonium antimonate, $NH_4SbO_3 \cdot 2H_2O$; ammonium iodate, HN_4IO_3 (2.6 grams per 100 ml. H_2O); ammonium chlorplatinate, $(NH_4)_2PtCl_6$ (0.67 gram); ammonium chloriridate, $(NH_4)_2IrCl_6$ (0.7 gram); ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$ (4.2 grams); ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12MoO_3$ (0.03 gram); nitron nitrate, $C_{20}H_{16}N_4 \cdot HNO_3$.

ORGANIC SUBSTANCES

By oxidation of nitrogenous organic substances with concentrated sulfuric acid, containing mercuric oxide, or potassium permanganate, the organic matter is destroyed and the nitrogen is changed to ammonia, which is held by the sulfuric acid as sulfate. Nitrates are reduced by addition of salicylic acid, zinc dust, etc., previous to the oxidation process. Practically all the procedures are based on the Kjeldahl method of acid digestion. The modification, commonly known as the Kjeldahl-Gunning-Arnold Method, is as follows:

Method in Absence of Nitrates. ***Weight of Sample.***—*Fertilizers* 0.7 to 3.5 grams. *Soils* 7 to 14 grams. *Meat* and *meat products* 2 grams. *Milk* 5 grams. The amount of the substance to be taken should be governed by its nitrogen content.[3]

Acid Digestion.[4]—The material is placed in a Kjeldahl flask of about 550 ml. capacity. Approximately 0.7 gram of mercuric oxide or an equivalent amount of metallic mercury together with 10 grams of powdered potassium sulfate followed by 20 to 30 ml. of concentrated sulfuric acid (sp.gr. 1.84) are added. The flask is placed in an inclined position, resting in a large circular opening of an asbestos board. The flask is heated with a small flame until the frothing has ceased. (A piece of paraffin may be added to prevent extreme frothing.) The heat is then raised and the acid brought to brisk boiling, the heating being continued until the solution becomes a pale straw color, or practically water white. (In case of leather, scrap, cheese, milk products, etc., a more prolonged digestion may be required. With a good flame from one-half to one hour of acid digestion is generally sufficient to completely decompose the material.) The flask is now removed from the flame and after cooling the solution is diluted with about 200 ml. of water and a few pieces of granulated zinc added to prevent "bumping" (50 mg. or so of No. 80 granulated zinc). The solution is now alkalized strongly by addition of a mixture of sodium hydroxide and sodium

[3] See data of approximate nitrogen content in certain nitrogenous substances, J. Ind. Eng. Chem., 7, 357, 1915.

[4] Figure 66 shows a compact apparatus with several sets of flasks and condensers, which enable half a dozen or more determinations to be made at one time.

sulfide solution (about 75 ml. of a mixture containing 25 grams of NaOH and 1 gram Na_2S). Phenolphthalein indicator added to the solution will show when the acid is neutralized. The flask is connected by means of a Hopkins distillation tube (Fig. 69) to a condenser and about 150 ml. of the solution distilled into an excess of standard sulfuric acid and the excess of the acid determined by titration with standard sodium hydroxide. (Methyl red indicator.)

The ammonia may be absorbed in a saturated solution of boric acid and titrated directly with standard acid. (Methyl red indicator.)[5]

One ml. N/10 H_2SO_4
$= 0.001703$ gram NH_3.

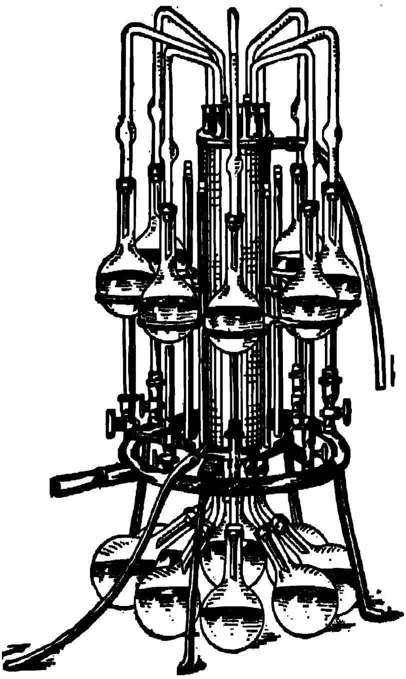


Fig. 66.—Apparatus for Determining Nitrogen.

In Presence of Nitrates.—The procedure differs from the former in the preliminary treatment to reduce the nitrates. The material in the flask is treated with a mixture of 30 to 35 ml. of conc. sulfuric acid containing 1 gram of salicylic acid and the mixture shaken and allowed to stand for five to ten minutes with frequent agitation. About 5 grams of sodium thiosulfate are now added and the solution heated for five minutes. After cooling, mercuric oxide or metallic mercury and potassium sulfate are added, and the solution treated as directed above. Reduced powdered iron may be used in place of salicylic acid for reducing nitrates.

Notes.—Mercuric oxide or metallic mercury are added as a catalyzer to assist the oxidation of the organic matter. The digestion process is shortened considerably by its use. In place of mercuric oxide or the metal, copper sulfate may be used. In this case the addition of sodium sulphide is omitted. Copper sulfate acts as an indicator in the neutralization of the sample with caustic.

Potassium sulfide is added to remove the mercury from the solution and prevent the formation of mercury-ammonium compounds, which are not completely decomposed by sodium hydroxide.

Ferric chloride, $FeCl_3$, may be used in place of copper or mercury salts or oxides to assist in the oxidation of organic matter.

Selenium Catalyst for Kjehldahl Digestions.—Lauro[6] reported that 0.1–0.2 g. of selenium in the form of oxychloride or the element itself might be used as a catalyst instead of the usual copper or mercury catalyst, with the advantage of a very considerable shortening of the period necessary for the conversion of the

[5] L. W. Winkler, Z. angew. Chem., 27, 1, 630, 1914. E. Bernard, *ibid.*, 27, 1, 664, 1914.

[6] Lauro, Ind. Eng. Chem., Anal. Ed. 3, 401 (1931).

nitrogen to ammonium salt and the destruction of the organic matter. The use of both selenium and mercuric oxide gives the same results for % N as the use of HgO alone and results in a 25% saving of time for various classes of materials.[7] A solution selenium dioxide in 1 : 1 H_2SO_4 is a convenient form in which to add the catalyst. 0.1–0.2 g. of selenium and 0.7 g. of HgO is a good combination catalyst for macro determinations.

Soils. Available Nitrates.—Five hundred to 1000 grams of the air-dried soil is extracted with 1 to 2 liters of water containing 10 to 20 grams of dextrose. Fifteen to twenty hours of leaching is sufficient. An aliquot portion is taken for analysis.

Ammonium Salts.—The sample is placed in the distillation flask with splash bulb as described in the modified Kjeldahl procedure for organic substances, and the material decomposed with ammonia-free caustic solution. The ammonia is distilled into an excess of standard acid or a saturated solution of boric acid (neutral to methyl orange), and the ammonia determined as usual, either by titration of the excess of acid, or by direct titration with acid, according to the absorbent used.

Nitrates.—The sample, broken down as fine as possible, is dissolved in water, decomposed with Devarda alloy and distilled as described by the modified Devarda methods given later.

Nitrites.—The material, dissolved in water, is titrated with standard permanganate solution according to the procedure described later.

Mixtures of Ammonium Salts, Nitrates and Nitrites.—Ammonia is determined by distillation with caustic as usual. The nitrite is titrated with permanganate. Total nitrogen is determined by the modified Devarda methods. Nitric acid is now estimated by difference, e.g., from the total nitrogen is deducted the nitrogen due to ammonia together with the nitrogen of the nitrite and the difference calculated to the nitrate desired. The nitrate may be determined in presence of nitrite and ammonia by direct titration with ferrous sulfate. The detailed procedures may be found under the Volumetric Methods.

Nitric Acid in Mixed Acid.—This is best determined by the ferrous sulfate method for nitric acid. The nitrometer method is also excellent.

NOTE.—P. H. Carter, Southern Fertilizer and Chemical Company,[8] recommends the following procedure:

Weigh the nitrate sample, put it into a Kjeldahl flask, then add 2 grams dry salicylic acid and the usual amount of potassium sulfate, mix well, by shaking the flask. Then add 5 ml. sulfuric acid (this gives a 40% salicylic acid concentration), this mixture is set aside a short time to insure proper solution and absorption, then add the remaining 25 ml. sulfuric acid and proceed with the regular method.

Dumas Method.—This method is discussed in treatises on the analysis of organic substances. A micro modification is given in the Chapter on Microanalysis, Vol. II.

[7] A critical comparison of the use of (1) Se catalyst; (2) HgO; (3) Se and HgO; (4) Se and $CuSO_4$ indicates that (3) is the most effective mixture for all varieties of material, according to Osborn and Krasnitz, J. Assoc. Official Agr. Chem., 16, 110 (1933); 17, 339 (1934). Other investigators report successful operation and saving of time either with Se alone of Se and $CuSO_4$ catalyst. See, for example: Illaraonov and Soloveva, Z. anal. Chem., 101, 254 (1935); Kurtz, Ind. Eng. Chem., Anal. Ed. 5, 260 (1933); Täufel, Thaler and Starke, Z. angew. Chem., 48, 191 (1935); Hartley, Ind. Eng. Chem., Anal. Ed. 6, 249 (1934).

[8] Chemist-Analyst, 19 (2), 15 (1930).

Ter Meulen Semi-micro Method.—References to the literature of this method are given in the Chapter on Carbon. In brief outline the method is as follows: The organic substance (20–50 mg.) is mixed with 1–2 g. of catalytic nickel and heated in a stream of hydrogen, and the partially hydrogenated material is passed over a 25 cm. packing of asbestos and nickel catalyst held at about 250° C. in a 1.5 cm. quartz combustion tube. The carbon is converted to methane, the oxygen to water and the nitrogen to NH_3. The latter is absorbed in standard acid and determined by titration.[9]

SEPARATIONS

Ammonia.—No special separation need be considered in the determination of ammonia. The general method has already been mentioned by which ammonia is liberated from its salts by a strong base and volatilized by heat. This effects a separation from practically all substances.

Nitric Acid.—The compound may be isolated as the fairly insoluble, crystalline nitron nitrate, $C_{20}H_{16}N_4 \cdot HNO_3$ by the following procedure.[10]

Such an amount of the substance is taken as will contain about 0.1 gram nitric acid, and dissolved in about 100 ml. of water with addition of 10 drops of dilute sulfuric acid. The solution is heated nearly to boiling and about 12 ml. of nitron acetate solution added (10 grams of nitron in 100 ml. of 50% acetic acid).[11] The solution is cooled and placed in an ice pack for about two hours, and the compound then transferred to a Gooch or Munroe crucible (weighed crucible if gravimetric method is to be followed), and after draining, it is washed with about 10 to 12 ml. of ice-water added in small portions. The nitrate may now be determined gravimetrically by drying the precipitate to constant weight at 110° C., 16.52% of the material being due to NO_3.

The base diphenyl-endo-anilo-hydro-triazole (nitron) also precipitates the following acids: nitrous, chromic, chloric, perchloric, hydrobromic, hydriodic, hydroferro- and hydroferricyanic, oxalic, picric and thiocyanic acids. Hence these must be absent from the solution if precipitation of nitric acid is desired for quantitative estimation.

Removal of Nitrous Acid.—Finely powdered hydrazine sulfate is dropped into the concentrated solution. (0.2 gram substance per 5 or 6 ml.)

Chromic acid is reduced by addition of hydrazine sulfate.

Hydrobromic acid is decomposed by chlorine water added drop by drop to the neutral solution, which is then boiled until the yellow color has disappeared.

Hydriodic acid is removed by adding an excess of potassium iodate to the neutral solution and boiling until the iodine is expelled.

[9] See Alsberg and Griffing, J. Am. Chem. Soc., 53, 1037 (1931), for details about the speed and accuracy of the method.

[10] M. Busch, Ber., 38, 861, 1905; Treadwell and Hall, "Analytical Chemistry."

[11] Keep nitron reagent in a dark-colored bottle.

PROCEDURES FOR THE DETERMINATION OF COMBINED NITROGEN

AMMONIA

The volumetric procedures for determination of ammonia are preferred to the gravimetric on account of their accuracy and general applicability. The following gravimetric method may occasionally be of use:

GRAVIMETRIC DETERMINATION OF AMMONIA BY PRECIPITATION AS AMMONIUM PLATINOCHLORIDE, $(NH_4)_2PtCl_6$

Ammonia in ammonium chloride may be determined gravimetrically by precipitation with chloroplatinic acid. The method is the reciprocal of the one for determining platinum.

Procedure.—The aqueous solution of the ammonium salt is treated with an excess of chloroplatinic acid and evaporated on the steam bath to dryness. The residue is taken up with absolute alcohol, filtered through a weighed Gooch crucible, and washed with alcohol. The residue may now be dried at 130° C. and weighed as $(NH_4)_2PtCl_6$, or it may be gently ignited in the covered crucible until ammonium chloride has been largely expelled and then more strongly with free access of air. The residue of metallic platinum is weighed. If the ignition method is to be followed, the ammonium platinic chloride may be filtered into a small filter, the paper with the washed precipitate placed in a porcelain crucible and then gently heated until the paper is charred (crucible being covered) and then more strongly with free access of air until the carbon has been destroyed.

Factors. $(NH_4)_2PtCl_6 \times 0.2409 = NH_4Cl$, or $0.08125 = NH_4$, or $\times 0.07671 = NH_3$. $Pt \times 0.5480 = NH_4Cl$, or $\times 0.1848 = NH_4$, or $\times 0.1745 = NH_3$.

VOLUMETRIC METHODS FOR DETERMINATION OF AMMONIA

Two conditions are considered:

A. Estimation of free ammonia in solution.

B. Determination of ammonia in its salts—combined ammonia.

ANALYSIS OF AQUA AMMONIA

Provided no other basic constituent is present, free ammonia in solution is best determined by direct titration with an acid in presence of methyl red indicator.

Procedure.—About 10 grams of the solution in a weighing bottle with glass stopper is introduced into an 800-ml. Erlenmeyer flask containing about 200 ml. of water and sufficient ½ normal sulfuric acid to combine with the ammonia and about 10 ml. in excess. The flask is stoppered and warmed gently. This forces out the stopper in the weighing bottle, the ammonia combining with the acid. Upon thorough mixing, the solution is cooled, and the excess of acid is titrated with half normal caustic.

One ml. ½ *N* $H_2SO_4 = 0.008516$ *gram* NH_3.

Factor. $H_2SO_4 \times 0.3473 = NH_3$.

NOTE.—The aqua ammonia exposed to the air will lose ammonia, hence the sample should be kept stoppered. This loss of ammonia is quite appreciable in conc. ammoniacal solutions.

DETERMINATION OF COMBINED AMMONIA. AMMONIUM SALTS

Strong bases decompose ammonium salts, liberating ammonia. This may be distilled into standard acid or into a saturated solution of boric acid (neutral to methyl orange) and titrated.

Procedure.—About 1 gram of the substance is placed in a distillation flask (see Fig. 66) and excess of sodium or potassium hydroxide added and the ammonia distilled into a saturated solution of boric acid or an excess of standard sulfuric acid. Ammonia in boric acid solution may be titrated directly with standard acid (methyl red indicator) or in case a mineral acid was used to absorb the ammonia, the excess of acid is titrated with standard caustic solution.

One ml. half normal sulfuric acid $= 0.0085$ gram NH_3.

One ml. normal acid $= 0.01703$ gram NH_3.

Factors. $H_2SO_4 \times 0.3473 = NH_3$ and $NH_3 \times 2.8793 = H_2SO_4$.

ANALYSIS OF AMMONIACAL LIQUOR

The crude liquor by-product from coal gas in addition to ammonia contains hydrogen sulfide, carbon dioxide, hydrochloric acid, sulfuric acid, combined with ammonia, also sulfites, thiosulfates, thiocyanates, cyanides, ferrocyanides, phenols.

DETERMINATION OF AMMONIA

Volatile Ammonia.—This is determined by distillation of the ammonia into an excess of standard sulfuric acid and titrating the excess of acid. With the exception that caustic soda is omitted in this determination, the details are the same as those for total ammonia as stated in the next paragraph.

Total Ammonia.—The true value of the liquor is ascertained by its total ammonia content. Ten to 25 ml. of the sample are diluted to about 250 ml. in a distilling flask with a potash connecting bulb, as previously described, 20 ml. of 5% sodium hydroxide are added and about 150 ml. of solution distilled into an

excess of sulfuric acid. The excess is then titrated according to the standard procedure for ammonia.

$$\text{One ml. N } H_2SO_4 = 0.01703 \text{ gram } NH_3.$$

Fixed Ammonia is the difference between the total and the volatile ammonia.

Carbon Dioxide

Ten ml. of the liquor are diluted to 400 ml. and 10 ml. of 10% ammoniacal calcium chloride added and the mixture, placed in a flask with Bunsen valve, is digested on the water bath for two hours. The precipitated calcium carbonate is washed, placed in a flask and an excess of N/2 HCl added and the excess acid titrated with N/2 NaOH.

$$\text{N/2 HCl} = 0.01100 \text{ gram } CO_2.$$

Hydrochloric Acid

Ten ml. of the liquor are diluted to 150 ml. and boiled to remove ammonia. Now hydrogen peroxide is added to oxidize organic matter, etc., the mixture being boiled to remove the excess of the peroxide. Chlorine is titrated in presence of potassium chromate as indicator by tenth normal silver nitrate after neutralizing with dilute nitric acid.

$$\text{One ml. N/10 } AgNO_3 = 0.003646 \text{ gram HCl.}$$

Hydrogen Sulfide

To 10 ml. of the liquor is added an excess of ammoniacal zinc chloride or acetate, the mixture diluted to about 80 ml. and warmed to 40° C. After settling for half an hour the zinc sulfide is filtered off and washed with warm water (40 to 50° C.); the precipitate is washed from the filter into an excess of N/10 iodine solution, the sulfide clinging to the paper washed into the main solution with hydrochloric acid. The mixture is acidified and the excess iodine titrated with N/10 sodium thiosulfate.

$$\text{One ml. N/10 I} = 0.001704 \text{ gram } H_2S \quad \text{or} \quad 0.001603 \text{ gram S.}$$

Sulfuric Acid

250 ml. of the liquor are concentrated to 100 ml., 2 ml. of concentrated hydrochloric added and the mixture heated to decompose any thiosulfate, sulfide or sulfite present. The concentrate is extracted with water, filtered and made to 250 ml. The sulfuric acid is now precipitated in an aliquot portion with barium chloride.

$$BaSO_4 \times 0.4202 = H_2SO_4, \quad \text{or} \quad \times 0.1373 = \text{S present as } H_2SO_4.$$

Total Sulfur.—Fifty ml. of the liquor are run by means of a pipette into a deep beaker (250 ml. capacity), containing an excess of bromine covered by

dilute hydrochloric acid. The mixture is evaporated to dryness on the steam bath and the residue taken up with water and diluted to 250 ml. Sulfur is now precipitated as barium sulfate as usual, preferably on an aliquot portion.

For a more complete analysis of crude liquor determining sulfite, thiosulfate, thiocyanate, hydrocyanic acid, ferrocyanic acid, and phenols the analyst is referred to Lunge, "Technical Methods of Chemical Analysis," Part II, Vol. II, D. Van Nostrand Co.

Determination of Traces of Ammonia

The determination of traces of ammonia is best accomplished by the colorimetric method with Nessler's reagent. Details of the procedure are given in the chapter on water analysis.

NITRIC ACID. NITRATES

The alkalimetric method for determining free nitric acid, and the complete analysis of the commercial product are given in the chapter on Acids. Special procedures for determining the combined acid are herein given.

GRAVIMETRIC METHOD FOR DETERMINING NITRIC ACID BY PRECIPITATION AS NITRON NITRATE, $C_{20}H_{16}N_4 \cdot HNO_3$

As in case of ammonia the volumetric methods are generally preferable for determining nitric acid, combined or free. Isolation of nitric acid by precipitation as nitron nitrate may occasionally be used. The fairly insoluble, crystalline compound, $C_{20}H_{16}N_4 \cdot HNO_3$ is formed by addition of the base diphenylendoanilo-hydro-triazole (nitron) to the solution containing the nitrate as directed under Separations. The precipitate washed with ice-water is dried to constant weight at 110° C. 16.52% of the compound is NO_3.

Note.—The following acids should not be present in the solution, since their nitron salts are not readily soluble: nitrous, chromic, chloric, perchloric, hydrobromic, hydriodic, hydroferrocyanic, hydroferricyanic, oxalic, picric and thiocyanic acids.

Solubility of less soluble nitron salts in 100 ml. of water. Nitron nitrate = 0.0099 gram, nitron bromide = 0.61 gram, iodide = 0.017 gram, nitrite = 0.19 gram, chromate = 0.06 gram, chlorate 0.12 gram, perchlorate = 0.008 gram, thiocyanate = 0.04 gram. (Treadwell and Hall, "Analytical Chemistry, Quantitative Analysis.")

COLORIMETRIC DETERMINATION [12]

Procedure.—A series of standards is prepared each containing 10 g. of potassium chloride and 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 2.0, 2.0, 4.0, 5.0 mg. of nitrate ion, respectively, per liter. To the aqueous solution of the nitrate to be analyzed is added potassium chloride to a concentration of 8–12 g. per liter. If one does not know the approximate concentration of the unknown, a preliminary experiment with standards containing 0.5, 1.0 and 3.0 mg. of nitrate per liter is run.

The mixtures are prepared in the following way: to 10 ml. of the nitrate-chloride solution is added 10 ml. of sulfuric acid from a pipette. Immediately after addition of the acid the flask is put into cold water and stirred sufficiently to mix its content. After cooling to room temperature 0.1 ml. of a 0.006 molar sodium diphenylamine sulfonate solution is added and the whole carefully mixed. The colors are compared in a colorimeter as soon as the more dilute of the two standards between which the unknown appears to belong has become sufficiently colored. There is no exact proportionality between intensity of color and nitrate concentration. Therefore the method of calculating the nitrate concentration of the unknown is an empirical one. Suppose the unknown was found between 2 and 3 mg.; then with the 3 mg. standard set at a reading of 20, the 2 mg. standard read 35 and the unknown 30. The concentration of the unknown then is equal to

$$2+\frac{35-30}{35-20}=2.33 \text{ mg. per liter}$$

After the preliminary series has given an approximate value the procedure just given is repeated with the unknown and its two closest standards. This determination gives an accuracy of the order of 5%.

VOLUMETRIC METHODS

DIRECT ESTIMATION OF NITRATES BY REDUCTION TO AMMONIA. MODIFIED DEVARDA METHOD [13]

An accurate procedure for the determination of nitrogen in nitrates is Allen's modification of the Devarda method. The method is based upon the quantitative reduction of nitrates to ammonia in an alkaline solution by an alloy con-

[12] I. M. Kolthoff and G. E. Noponen, J. Am. Chem. Soc., 55, 1448 (1933).
[13] W. S. Allen, Eighth International Congress of Applied Chemistry.

sisting of 45 parts of aluminum, 50 parts of copper and 5 parts of zinc. The ammonia evolved is distilled into standard sulfuric acid and thus estimated. The method, originally designed for the valuation of sodium or potassium nitrates, is also of value in the determination of nitric acid, nitrites or ammonia. In the latter case the alloy is omitted.

Reagents Required. *Devarda's Alloy.*—Forty-five parts aluminum, 50 parts copper and 5 parts zinc. The aluminum is heated in a Hessian crucible in a furnace until the aluminum begins to melt, copper is now added in small portions until liquefied and zinc now plunged into the molten mass. The mix is heated for a few moments, covered and then stirred with an iron rod, allowed to cool slowly with the cover on and the crystallized mass pulverized.

Standard Sulfuric Acid.—This is made from the stock C.P. acid by dilution so that 1 ml. is equal to 0.0057 gram H_2SO_4, 100 ml. of acid of this strength being equivalent to approximately 1 gram of sodium nitrate. (A tenth normal acid will do, a smaller sample being taken for analysis.) Since it is necessary to standardize this acid against a standard nitrate, it is advisable to have an acid especially for this determination rather than a common reagent for general use.

Standardization of the Acid.—11.6 grams of standard potassium nitrate, equivalent to about 9.6 grams of $NaNO_3$, is dissolved and made to volume in the weighing bottle (100 ml.), and 10 ml. is placed in the Devarda flask, reduced and the ammonia distilled into 100 ml. of the acid, exactly as the following method describes. The temperature of the acid is noted and its value in terms of H_2SO_4, KNO_3 and $NaNO_3$ stated on the container. The acid expands or contracts 0.029 ml. per 100 ml. for every degree centigrade above or below the temperature of standardization.

Standard Potassium Nitrate.—The purest nitrate that can be obtained is recrystallized in small crystals, by stirring, during the cooling of the supersaturated concentrated solution, and dried first at 100° C. for several hours and then at 210° C. to constant weight. Chlorides, sulfates, carbonates, lime, magnesia and sodium are tested for and if present are determined and allowance made.

Standard Sodium Hydroxide.—This should be made of such strength that 1 ml. is equal to 1 ml. of the standard acid, 2 ml. methyl red being used as indicator. Ten ml. of the acid are diluted to 500 ml. and the alkali added until the color of the indicator changes from a red to a straw color.

Methyl Red Solution.—0.25 gram of methyl red is dissolved in 2000 ml. of 95% alcohol; 2 ml. of the indicator is used for each titration. As the indicator is sensitive to CO_2, all water used must first be boiled to expel carbonic acid.

Sodium Hydroxide—Sp.gr. 1.3.—Pure sodium hydroxide is dissolved in distilled water and boiled in an uncovered casserole with about 1 gram of Devarda's alloy to remove ammonia. This is cooled and kept in a well-stoppered bottle.

Apparatus.—This is shown in the accompanying illustration, Fig. 67. It consists of the Devarda flask connected to the scrubber *K*, filled with glass wool. This scrubber is heated by an electric coil or by steam passed into the surrounding jacket. The scrubber prevents caustic spray from being carried over into the receiving flask *O*. The form of the apparatus can best be ascertained from the sketch.

Weighing bottle with graduation at 100 ml. and a 10-ml. dropper with rubber bulb is used for weighing out the sample in solution. See Fig. 68.

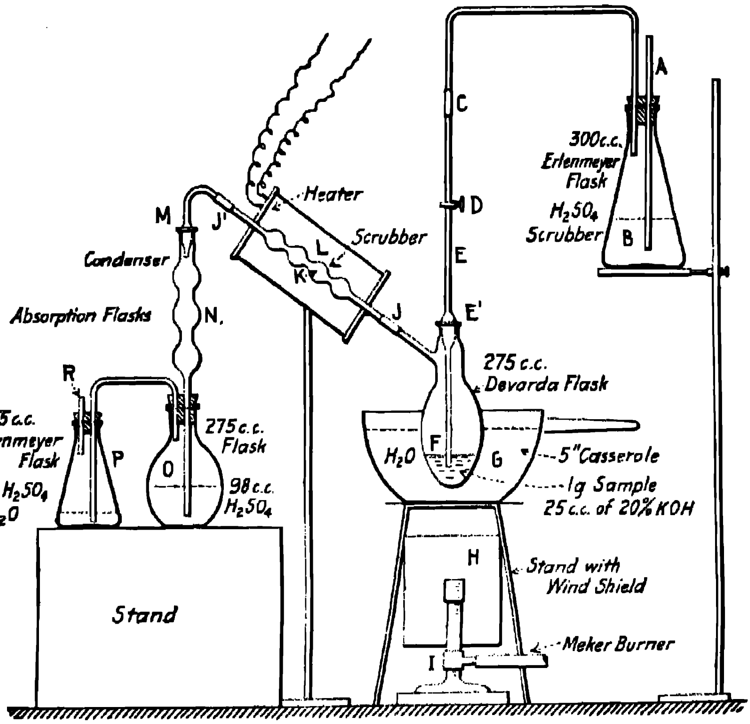


FIG. 67.—Devarda's Apparatus.

PREPARATION OF THE SAMPLE

Weight.—It is advisable to take a large sample if possible, e.g., 100 grams of $NaNO_3$, 119 grams of KNO_3 or about 80 grams of conc. HNO_3 (95%) or more if the acid is dilute. Solids are taken from a large sample, all lumps being broken down. After dissolving in water the sample is made up to 1 liter. (Scum is broken up by addition of a little alcohol.) One hundred ml. of this solution is placed in the weighing bottle, which has been previously weighed, being perfectly clean and dry. The difference is the weight of the 100-ml. sample.

Manipulation.—All parts of the apparatus are washed out with CO_2-free water. All water used in this determination should be boiled to expel CO_2. Ninety-eight ml. of the standard acid is placed in flask *O* and washed down with 2 to 3 ml. of water. Two ml. of the standard acid are placed in flask *P* and washed down with 10 ml. of water and 13 to 14 drops of methyl red indicator added. Connections are made between the flasks and the scrubber. (The correction is made for the acid, the temperature being noted at the time of withdrawal.) A casserole, filled with cold water, is placed under *F* (see illustration). The stem *E* is removed from the Devarda flask and 10 ml. (or more) of the nitrate added by means of the dropper in the weighing bottle, a funnel hav-

ing been inserted in the flask. The bottle reweighed gives the weight of the sample removed, by difference. The nitrate is washed down with 10 ml. of water and 25 ml. of 20% caustic added (free from NH_3), the alkali washed down with 10 ml. more of water and then 3 grams of Devarda alloy placed in the flask by means of dry funnel. The stem *E* is quickly replaced, the stopcock being turned to close the tube. The reaction begins very soon. If it becomes violent, the reaction may be abated by stirring the water in the casserole, thus cooling the sample. After the energetic action has abated (five minutes), the casserole with the cold water is removed and the action allowed to continue for twenty minutes, meantime heat or steam is turned on in the scrubber. *E* is connected at *C* to the flask *B* containing caustic to act as a scrubber. It is advisable to have a second flask containing sulfuric acid attached to the caustic to prevent ammonia from the laboratory entering the system. A casserole with hot water is placed under *F* and the burner lighted and turned on full. A gentle suction is now applied at *R*, the stop-cock *D* being turned to admit pure air into the evolution flask; the rate should be about 5 to 6 bubbles per second. The suction is continued for thirty minutes, hot water being replaced in the casserole as the water evaporates. The heat is now turned off and the apparatus disconnected at *M* and *J*. The contents of this elbow and the condenser are washed into the flask *O*. The acid in *O* and *P* poured into an 800-ml. beaker and rinsed out several times. The volume in the beaker is made up to 500 ml., 1 ml. of methyl red added, and the free acid titrated with the standard caustic. The end-point is a straw yellow.

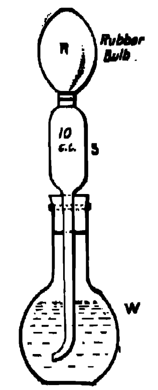


FIG. 68.—Weighing Bottle and Dropper.

Calculation.—The ml. of the back titration with caustic being deducted, the volume of the acid remaining (e.g., combined with ammonia) is corrected to the standard condition. Expansion or contraction per 100 ml. is 0.029 ml. per each degree C. above or below the temperature at which the acid was standardized. If the acid is exactly 0.057 gram H_2SO_4 per ml., the result multiplied by 0.989 and divided by the weight of the sample taken gives % nitrate. (In terms of $NaNO_3$.)

The Weight of the Sample.—Ten times the difference of the weighings of the bottle *W* before and after removal of the 10 ml. and the product divided by the weight of the 100 ml. of the solution equals the weight of solid taken.

Example.—*Weight* of the bottle +100 ml. sample =218 grams. Weight of the bottle =112 grams, therefore weight of 100 ml. $NaNO_3$=106 grams.

Weight of the bottle +100 ml. sample =218. Weight after removal of 10 ml. =207.4 grams, therefore sample taken =10.6 grams, including the added water. Now from above the weight of the actual sample taken =10.6×10÷106=1 gram.

Temperature Correction.—Temperature of standardization =20° C. Temperature of the sulfuric acid when taken for the analysis =31° C. Back titration of the caustic =2 ml. The correct volume =(100−2)−((31−20)×0.029)=97.681 ml. H_2SO_4 combined with ammonia from the reduced nitrate. 97.681×0.989÷1=96.62% $NaNO_3$.

Factors. H_2SO_4×2.0618=KNO_3 or ×1.7335=$NaNO_3$ or ×1.2851=HNO_3.

H_2SO_4×0.9588=HNO_2 or ×0.3473=NH_3.

NH_3×3.7001=HNO_3 or ×4.9913=$NaNO_3$ or ×4.0517=$NaNO_2$.

$NaNO_3$×1.1894=KNO_3 and KNO_3×0.8408=$NaNO_3$.

THE VOLUMETRIC DETERMINATION OF NITRATES WITH FERROUS SULFATE AS REDUCING AGENT[14]

Procedure.—A 0.1–0.2-g. sample of nitrate is introduced into the 250 ml. Erlenmeyer flask; 25 or 50 ml. 0.18 N ferrous iron solution are added (an excess of approximately 50% of ferrous iron is recommended) and 70 ml. 12 N hydrochloric acid. Then 3 to 5 g. of solid sodium bicarbonate is added carefully in small portions to displace the air from the flask and immediately thereafter the flask is closed with the stopper, from which a rubber tube leads to a suspension to 50 g. of sodium bicarbonate in 100 ml. of water. The dropper fitted into the other hole of the stopper contains 3 ml. of 1% ammonium molybdate solution. The solution is heated and the catalyst added after two or three minutes' boiling. The boiling is continued for ten minutes, the sodium bicarbonate suspension then replaced with a fresh saturated solution, the flask removed from the flame and immersed in cold water. After cooling to room temperature the flask is unstoppered and 35 ml. of 6 N ammonium acetate for every 50 ml. of solution to be titrated and 3 to 5 ml. 85% phosphoric acid are added. The acetate reduces the concentration of the strong acid to between 1 and 2 N. The solution, which should have a volume of 100 to 150 ml., is slowly titrated with 0.1 N dichromate using 6 to 8 drops of diphenylamine sulfonate (or diphenylamine or diphenylbenzidine) as indicator. The ferrous iron solution is standardized under the same conditions as described above.

One ml. of 0.1000 N iron is equivalent to 3.370 mg. of potassium nitrate or 2.067 mg. of NO_3.

ANALYSIS OF NITRATE OF SODA

The following impurities may occur in nitrate of soda: KNO_3, NaCl, Na_2SO_4, Na_2CO_3, $NaClO_3$, $NaClO_4$, Fe_2O_3, Al_2O_3, CaO, MgO, SiO_2, H_2O, etc. In the analysis of sodium nitrate for determination of $NaNO_3$ by difference, moisture, NaCl, Na_2SO_4 and insoluble matter are determined and their sum deducted from 100, the difference being taken as $NaNO_3$. Such a procedure is far from accurate, the only reliable method being a direct determination of niter by the Devarda method given in detail. The following analysis may be required in the valuation of the nitrate of soda.

DETERMINATION OF MOISTURE

Twenty grams of sample are heated in a weighed platinum dish at 205 to 210° C. for fifteen minutes in an air bath or electric oven. The loss of weight multiplied by 5 = % moisture. (Save sample for further tests.)

[14] I. M. Kolthoff, E. B. Sandell and B. Moskovitz, J. Am. Chem. Soc., 55, 1454 (1933).

INSOLUBLE MATTER

Ten grams are treated with 50 ml. of water and filtered through a tared filter crucible. The weight of the dried residue (100° C.) multiplied by 10 = % insoluble matter. (Save filtrate.)

SODIUM SULFATE

The moisture sample is dissolved in 20 ml. hot water and transferred to a porcelain crucible. It is evaporated several times with hydrochloric acid to dryness to expel nitric acid. (Until no odor of free chlorine is noticed when thus treated.) Fifty ml. of water and 5 ml. hydrochloric acid are now added and the sample filtered. Any residue remaining is principally silica. The filtrate is heated to boiling, 10 ml. of 10% barium chloride solution added, and the precipitated sulfate filtered off, ignited and weighed.

$$BaSO_4 \times 3.0429 = \%\ Na_2SO_4.$$

IRON, ALUMINA, LIME, AND MAGNESIA

These impurities may be determined on a 20-gram dried sample, the material being dried and evaporated as in case of the sodium sulfate determination. The filtrate from silica is treated with ammonium hydroxide and $Fe(OH)_3$ and $Al(OH)_3$ filtered off. Lime is precipitated from the iron and alumina filtrate as oxalate and magnesia determined by precipitation as phosphate from the lime filtrate by the standard procedures.

SODIUM CHLORIDE

The filtrate from the insoluble residue is brought to boiling and magnesia, MgO (Cl free), is added until the solution is alkaline to litmus. 0.5 ml. of 1% potassium chromate (K_2CrO_4) solution is added as an indicator and then the solution is titrated with a standard solution of silver nitrate until a faint red tinge is seen, the procedure being similar to the determination of chlorides in water by silver nitrate titration. The ml. $AgNO_3 \times$ factor for this reagent $\times 10$ = % NaCl.

Silver nitrate is standardized against a salt solution.

CARBONATES

This determination is seldom made. CO_2 may be tested for by addition of dilute sulfuric acid to the salt. Effervescence indicates carbonates. Any evolved gas may be tested by lime water, which becomes cloudy if CO_2 is present. For details of the procedure reference is made to the chapter on Carbon.

DETERMINATION OF NITRIC NITROGEN IN SOIL EXTRACTS

VAMARI-MITSCHERLICH-DEVARDA METHOD

Procedure.—Forty ml. of water, a small pinch of magnesia and one of magnesium sulfate are added to flask *D* of the Mitscherlich apparatus (Fig. 69). Twenty-five ml. of standard acid and 60 ml. of neutral redistilled water are placed in flask *F*; 250 or 300 ml. of aqueous soil extract are placed in a 500-ml. Kjeldahl flask, 2 ml. of 50% sodium hydroxide added, the mouth of the flask closed with a small funnel to prevent spattering, and the contents of the flask boiled for thirty minutes. The water which has boiled off is replaced, and, after cooling, 1 gram of Devarda's alloy (60 mesh), and a small piece of paraffin are added and the flask connected with the apparatus; reduction and distillation are carried on for forty minutes. The receiver contents are then cooled, 4 drops of 0.02% solution of methyl red added, the excess acid is nearly neutralized, the liquid boiled to expel CO_2, cooled to 10 to 15° C. and the titration completed.

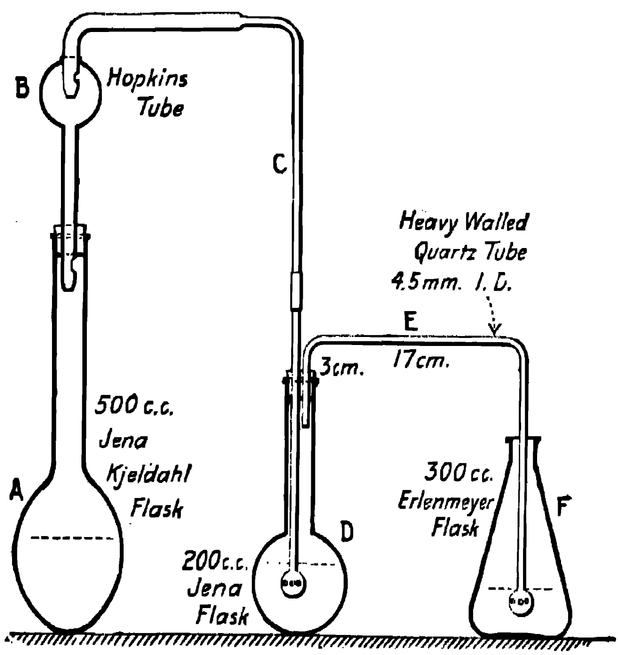


Fig. 69.—Mitscherlich's Apparatus for Nitrogen Determination.

B. S. Davisson,[15] recommends an improved form of scrubber, shown in Fig. 70 to be used in place of the Hopkins bulb (Fig. 69). The bulb and adaptor are made of Pyrex glass. Steam condenses in the bulb and the condensate acts as a scrubber preventing alkali mist from being carried over with the ammonia. During the test ammonia is completely volatilized into the absorption flask. The bulb of the adaptor prevents back suction into the distillation flask.

[15] Reference B. S. Davisson, J. Ind. Eng. Chem., 11, 465, 1919

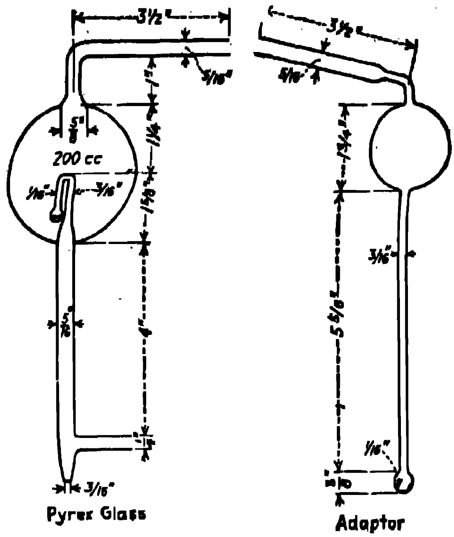


FIG. 70.—Davisson's Scrubber.

DETERMINATION OF HYDROXYLAMINE—METHOD OF RASCHIG [16]

Hydroxylamine in hot acid solutions reduces ferric salts to ferrous condition quantitatively according to the reaction:

$$2NH_2OH+2Fe_2(SO_4)_3=4FeSO_4+2H_2SO_4+N_2O+H_2O.$$

The amount of ferrous iron formed is a measure of the hydroxylamine originally present.

Procedure.—Approximately 0.1 gram of hydroxylamine salt is dissolved in a little water in an Erlenmeyer flask and 30 ml. of cold saturated solution of ferric-ammonium alum added, followed by 10 ml. of dilute sulfuric acid (1 : 4). The solution is heated to boiling and kept at this temperature for five minutes, then diluted to 300 ml. and titrated immediately with standard permanganate solution.

$$\text{One ml. } N/10\ KMnO_4=0.001652\text{ g. } NH_2OH.$$

IODOMETRIC DETERMINATION OF NITRATES—METHOD OF GOOCH AND GRUENER [17]

By this method the nitrate to be estimated is treated, in an atmosphere of carbon dioxide, with a saturated solution of manganous chloride (crystallized)

[16] Hydroxylamine may also be determined by reduction with an excess of titanous salt in acid solution with exclusion of air, and the excess titrated with permanganate.

$$\text{Reaction: } 2NH_2OH+Ti_2(SO_4)_3=(NH_4)_2SO_4+4TiOSO_4+H_2SO_4.$$

For discussion of the two methods see paper by Wm. C. Bray, Miriam E. Simpson and Anna A. MacKenzie, J. Am. Chem. Soc., 41, 9, 1362, 1919.

[17] "Methods in Chemical Analysis," by F. A. Gooch. F. A. Gooch and H. W. Gruener, Am. J. Sci. (3), **44**, 117, 1892.

in concentrated hydrochloric acid, the volatile products of the reaction (nitrogen dioxide, chlorine, etc.) are now distilled and caught in a solution of potassium iodide. The iodine set free is titrated by a standard solution of thiosulfate.

Procedure.—The nitrate and the manganous mixture (saturated solution of crystallized manganous chloride and conc. hydrochloric acid—20 ml. per 0.2 gram sample) following it are introduced into the pipette shown in Fig. 71 (marked III) suction being applied, if necessary, at the end of the absorption train (VI). The current of CO_2 is started immediately after putting in the mixture. When the air has been replaced by CO_2, heat is applied to the retort III and the distillation continued until nearly all the liquid has passed over into the receiver IV, which is cooled by water. (See illustration.) The contents of the receivers are united and the bulbs washed out by passing the wash water directly through III and IV. Introduction of manganous chloride into the distillate does not influence the accuracy of the titration. The liberated iodine is titrated with standard sodium thiosulfate as soon as possible after admitting air to the distillate, since traces of dissolved nitric oxide reoxidized by the air would react with the iodide liberating more iodine.

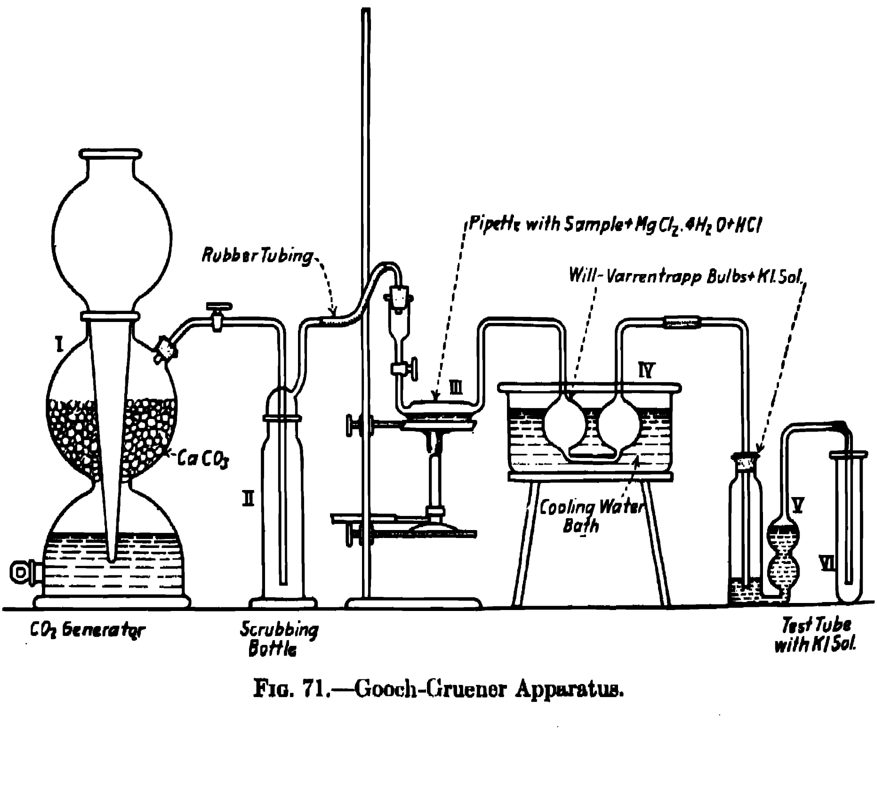


FIG. 71.—Gooch-Gruener Apparatus.

DETERMINATION OF NITROGEN OF NITRATES (AND NITRITES) BY MEANS OF THE NITROMETER

The nitrometer is an exceedingly useful instrument employed in the accurate measurement of gases liberated in a great many reactions and has therefore a number of practical applications. It may be used in the determination of carbon dioxide in carbonates; the available oxygen in hydrogen dioxide; in the valuation of nitrous ether and nitrites; in the valuation of nitrates and nitric acid in mixed acids.

The method for the determination of nitrogen in nitrates, with which we are concerned in this chapter, depends on the reaction between sulfuric acid and nitrates in presence of mercury:

$$2KNO_3+4H_2SO_4+3Hg=K_2SO_4+3HgSO_4+4H_2O+2NO.$$

The simplest type of apparatus is shown in the illustration, Fig. 72. The graduated decomposition tube has a capacity of 100 ml. It is connected at the base by means of a heavy-walled rubber tubing with an ungraduated leveling tube (*b*). At the upper portion of (*a*) and separated from it by a glass stop-cock (*s*) is a bulb (*c*) of about 5 ml. capacity; a second stop-cock enables completely enclosing the sample, as may be necessary in volatile compounds. The glass stop-cock (*s*), directly above the graduated chamber, is perforated so as to establish connection with the tube (*d*) when desired and the graduated cylinder (*a*).

Procedure.—The tube (*b*) is filled with mercury and the air in (*a*) now displaced by mercury, by turning the stop-cock to form an open passage between (*a*) and (*d*) and then raising (*b*). A sample of not over 0.35 gram potassium nitrate or a corresponding amount of other nitrates, is introduced into (*c*), the material being washed in with the least amount of water necessary (1 to 2 ml.). By lowering (*b*) and opening the stop-cock *s* the solution is drawn into the decomposition chamber, taking care that no air enters. This is followed by about 15 ml. of pure, conc. sulfuric acid through s_1 and *s*, avoiding admitting air as before. NO gas is liberated by the heat of reaction between the sulfuric acid and the water solution. When the reaction subsides, the tube (*a*) is shaken to mix the mercury with the liquor and the NO completely liberated. The gas is allowed to cool to room temperature and then measured, after raising or lowering (*b*) so that the column of mercury is the calculated excess of height above that in (*a*) in order to have the gas under atmospheric pressure. The excess of height is obtained by dividing the length of the acid layer in (*a*), in millimeters, by 7 and elevating the level of the mercury in (*b*) above that in (*a*) by this quotient; i.e., if the acid layer=21 mm. the mercury in (*b*) would be 3 mm. above that in (*a*). The volume of gas is reduced to standard conditions by using the formula

$$V'=\frac{V(P-w)}{760(1+0.00367t)}.$$

V'= volume under standard conditions; V= observed volume; P= observed barometric pressure in mm.; w= tension of aqueous vapor at the observed temperature, expressed in millimeters; t= observed temperature.

One ml. gas = 4.62 milligrams of KNO_3, or 3.8 milligrams $NaNO_3$ or 2.816 milligrams HNO_3.

DU PONT NITROMETER METHOD[18]

The Du Pont nitrometer, Fig. 73, is the most accurate apparatus for the volumetric determination of nitrates. By use of this, direct readings in % may be obtained, without recourse to correction of the volume of gas to standard conditions and calculations such as are required with the ordinary nitrometers.

The apparatus consists of a generating bulb of 300 ml. capacity E with its reservoir F connected to it by a heavy-walled rubber tubing. E carries two glass stop-cocks as is shown in illustration. The upper is a two-way stop-cock connecting either the cup or an exit tube with the chamber. D is the chamber-reading burette, calibrated to read in percentages of nitrogen, and graduated from 10 to 14%, divided in 1/100%. Between 171.8 and 240.4 ml. of gas must be generated to obtain a reading. A is also a measuring burette, that may be used in place of D where a wider range of measurement is desired. " It is used for the measurement of small as well as large amounts of gas. It is most commonly graduated to hold 300.1 milligrams of NO at 20° C. and 760 mm. pressure and this volume is divided into 100 units (subdivided into tenths) each unit being equivalent to 3.001 milligrams of NO. When compensated, the gas from ten times the molecular weight in milligrams of any nitrate of the formula RNO_3 (or five times molecular weight of $R(NO_3)_2$) should exactly fill the burette. This simplifies all calculations; for example the % nitric acid in a mixed acid would be

$$\frac{R63.02}{100W} = \%\ HNO_3.$$

R = burette reading, W = grams acid taken."[19] C is the compensating burette very similar in form to the chamber burette D. B is the leveling bulb, by the raising or lowering of which the standard pressure in the system may be obtained. The apparatus as shown in Fig. 73 is mounted on an iron stand. As in the more simple form of apparatus, previously described, mercury is used as the confining liquid. The parts are connected by heavy-walled rubber tubing, wired to the glass parts.

Standardizing the Apparatus.—The apparatus having been arranged and the various parts filled with mercury, the instrument is standardized as follows: 20 to 30 ml. of sulfuric acid are drawn into the generating bulb through the cup at the top, and at the same time about 210 ml. of air; the cocks are then closed, and the bulb well shaken; this thoroughly desiccates the air, which is then run over into the compensating burette until the mercury is about on a level with the 12.30% mark on the other burette, the two being held in the same relative position, after which the compensating burette is sealed off at the top. A further quantity of air is desiccated in the same manner and run into the reading burette so as to fill up to about the same mark; the cocks are then closed, and a small piece of glass tubing bent in the form of a U, half filled with sulfuric acid (not water), is attached to the outlet of the reading burette; when the mercury columns are balanced and the enclosed air cooled down, the cock is again carefully opened, and when the sulfuric balances in the U-tube, and the mercury

[18] See paper by J. R. Pitman, J. Soc. Chem. Ind., 19, 983, 1900.

[19] A. W. Betts, Chemist, E. I. DuPont de Nemours Powder Co., private communication.

columns in both burettes are at the same level, then the air in each one is under the same conditions of temperature and pressure. A reading is now made from the burette, and the barometric pressure and temperature carefully noted, using the formula

$$V_t = \frac{V_0 P_0 (273+t)}{P_t 273},$$

the volume this enclosed air would occupy at 29.92 ins. pressure and 20° C. is found. The cock is again closed and the reservoir manipulated so as to bring

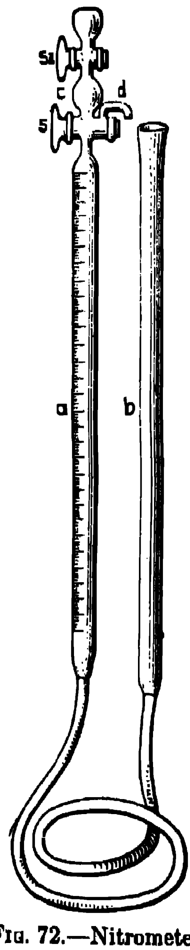


Fig. 72.—Nitrometer.

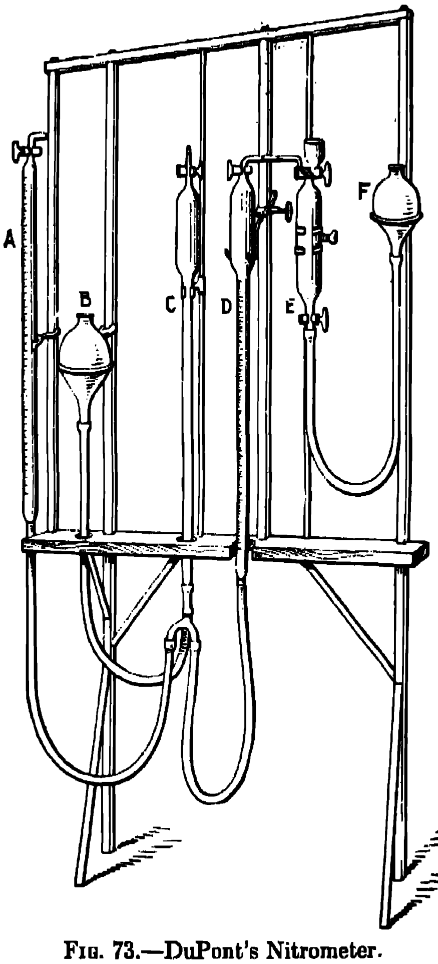


Fig. 73.—DuPont's Nitrometer.

the mercury in both burettes to the same level, and in the reading burette to the calculated value as well. A strip of paper is now pasted on the compensating burette at the level of the mercury, and the standardization is then complete.

Another rapid method of standardizing is to fill the compensating chamber with desiccated air as stated in the first procedure and then to introduce into the generating chamber 1 gram of pure potassium nitrate dissolved in 2 to 4 ml. of

water, the cup is rinsed out with 20 ml. of 66° Béaume sulfuric acid, making three or four washings of it, each lot being drawn down separately into the bulb. The generated gas formed after vigorous shaking of the mixture, as stated under procedure, is run into the measuring burette. The columns in both burettes are balanced so that the reading burette is at 13.85 (= % N in KNO_3). A strip of paper is pasted on the compensating burette at the level of the mercury, and standardization is accomplished. By this method the temperature and pressure readings, and the calculations are avoided.[20]

Procedure for Making the Test. *Salts.*—One gram of sodium or potassium nitrate, or such an amount of the material as will generate between 172 to 240 ml. of gas, is dissolved in a little water and placed in the cup of the generating bulb.

Liquid Acids.—The acid is weighed in a Lunge pipette and the desired amount run into the funnel of the generating bulb, the amount of acid that is taken being governed by its nitrogen content.

The sample is drawn into the bulb; the funnel is then rinsed out with three or four successive washings of 95% sulfuric acid, the total quantity being 20 ml.

To generate the gas, the bulb is shaken well until apparently all the gas is formed, taking care that the lower stop-cock has been left open, this cock is then closed and the shaking repeated for two minutes. The reservoir is then lowered until about 60 ml. of mercury and 20 ml. of acid are left in the generating bulb. There will remain then sufficient space for 220 ml. of gas.

NOTE.—If too much mercury is left in the bulb, the mixture will be so thick that it will be found difficult to complete the reaction, a long time will be required for the residue to settle and some of the gas is liable to be held in suspension by the mercury, so that inaccurate results follow.

The generated gas is now transferred to the reading burette, and after waiting a couple of minutes to allow for cooling, both burettes are balanced, so that in the compensating tube the mercury column is on a level with the paper mark as well as with the column in the reading burette; the reading is then taken.

If exactly one gram of the substance is taken the percentage of nitrogen may be read directly, but in case of other amounts being taken, as will invariably be the case in the analysis of acids, the readings are divided by the weight of the substance and multiplied by 4.5 to obtain the per cent of nitric acid monohydrate present.

The procedure may be used for determining nitrites as well as nitrates.

DETERMINATION OF HNO_3 IN OLEUM BY DU PONT NITROMETER METHOD[21]

About 10 ml. oleum are weighed in a 30-ml. weighing bottle, 10 ml. 95% reagent sulfuric acid added and mixed by shaking. This mixture is transferred to the nitrometer reaction tube and the weighing bottle and nitrometer cup rinsed with three 5-ml. portions of the reagent sulfuric acid which is drawn into

[20] Standardization with "C. P. KNO_3 is the better, as it is less tedious and is not subject to the correction errors that cannot be escaped when standardizing with air. The KNO_3 must be of undoubted purity."—A. W. Betts.

[21] By courtesy of E. I. du Pont de Nemours Powder Co.

the reaction tube. This is vigorously shaken for three minutes and the gas then passed to the measuring tube and allowed to stand for about five minutes, after which the mercury levels are adjusted and the reading taken.

It is obvious that this determination includes any nitrous acid in the oleum.

COMBINED NITRIC ACID

The nitric acid in nitrates may be determined by titration with ferrous sulfate. The nitrate dissolved in a little water is run into conc. sulfuric acid and titrated with standard ferrous sulfate according to the procedure described for determining free nitric acid in mixed acids (Vol. II, Acids).

DETERMINATION OF FREE NITRIC ACID

Other acids being absent, free nitric acid may be determined by titration with standard alkali. Details for the analysis of nitric acid in presence of commonly occurring impurities are given in Volume II in the chapter on Acids.

One ml. N/1 $NaOH = 0.063016$ g. HNO_3.

DETERMINATION OF NITRITES

GRAVIMETRIC METHOD OF BUOVOLD [22]

One and one-fourth to 1.5 grams of $AgBrO_3$ are dissolved in 100 ml. of water and 110 ml. of 2 N acetic acid, in an Erlenmeyer flask. Two hundred ml. of the nitrite solution (1 g. $NaNO_2$) are added from a burette, stirring the mixture during addition of the nitrite. A pale green precipitate is obtained. Thirty ml.of H_2SO_4 (1 : 4) are added, the mixture warmed to 85° C. When the yellow precipitate settles it is filtered on a Gooch and washed with hot water, then dried and weighed as $AgBr+AgCl$ – chlorine is determined on a separate portion and AgCl deducted. $AgBr \times 0.9070 = NaNO_2$. The method is specially applicable to nitrites high in chlorine.

VOLUMETRIC PERMANGANATE METHOD

Principle.—Potassium permanganate reacts with nitrous acid or a nitrite as follows:

$$5N_2O_3+4KMnO_4+6H_2SO_4=5N_2O_5+2K_2SO_4+4MnSO_4+6H_2O.$$

$$5HNO_2+2KMnO_4+3H_2SO_4=5HNO_3+K_2SO_4+2MnSO_4+3H_2O.$$

[22] Chem. Ztg., 38, 28 (1914). C. A. 8, 1250, 1914.

Since $2KMnO_4$ in acid solution has five available oxygens for oxidation of substances (e.g., $2KMnO_4 = K_2O \cdot 2MnO + 5O$ equivalent to 10H) the molecular weights of the constituents divided by 20 in the first equation and by 10 in the second would represent the normal weights per liter, e.g., $5N_2O_3$ divided by 20=76 divided by 4=19 grams N_2O_3 per liter. $4KMnO_4$ divided by 20 or $2KMnO_4$ divided by 10=158.03 divided by 5=31.61 grams of $KMnO_4$ per liter for a normal solution. In the second equation if Na represents the univalent element we would have $5NaNO_2$ divided by 10 or 69 divided by 2=34.5 grams per liter. Hence 1 ml. of a normal $KMnO_4$ solution would oxidize 0.019 gram N_2O_3 or 0.0345 gram $NaNO_2$ to form N_2O_5 and $NaNO_3$ respectively.

Organic matter is also oxidized by $KMnO_4$ hence will interfere if present.

Special Reagents. ***N/5 Potassium Permanganate.***—The solution contains 6.322 grams $KMnO_4$ per liter.

N/5 Sodium Oxalate.—$Na_2C_2O_4$ reacts with $KMnO_4$ as follows:

$$5Na_2C_2O_4+2KMnO_4+8H_2SO_4=K_2SO_4+2MnSO_4+5Na_2SO_4+10CO_2+8H_2O.$$

Hence $5Na_2C_2O_4$ divided by 10 or 134 divided by 2=67 grams per liter = a normal sodium oxalate solution. A N/5 solution requires 13.4 grams $Na_2C_2O_4$ per liter.

Preparation of the Sample

Soluble Nitrites.—Ten grams of the nitrite are dissolved in water and made to 1000 ml.; 10 ml. contain 0.1 gram of the sample.

Water-insoluble Nitrites.—0.5 to 1.0 gram of the nitrite according to the amount of nitrous acid present is taken for analysis. An excess of $KMnO_4$ solution is added, followed by dilute H_2SO_4 and the excess standard permanganate titrated with sodium oxalate according to directions given under Procedure.

Nitrous Acid in Nitric Acid and Mixed Acids.—This is present generally in very small amounts so that a large sample is taken. The amount and details of the procedures are given under the special subject.

For routine work where a number of daily determinations are made, a 50-ml. burette is generally preferred.

Trial Run.—If the approximate strength of the salt is not known the following test may be quickly made to ascertain whether more than 50 ml. of solution is necessary and the approximate amount of $KMnO_4$ required for oxidation.

Ten ml. of the solution together with 100 ml. of water are placed in a 4-in. casserole and about 10 ml. of dilute H_2SO_4, 1 : 1, added. Standard $KMnO_4$ from a 50-ml. burette is now run into the sample until a permanent pink color is obtained. The ml. of $KMnO_4$ multiplied by 5=the approximate amount of permanganate solution required for oxidation of 50 ml. of sample. An excess of 5 to 10 ml. should be taken in the regular run.

Titration of Nitrite.—Sufficient standard N/5 $KMnO_4$ to oxidize the sample to be titrated (as ascertained by the trial run) and 10 ml. excess are placed in a casserole. The solution is acidified with 10 ml. of dilute (1 : 4) H_2SO_4 and 50 ml. of the nitrite solution is added slowly with constant stirring. The sample is placed on a hot plate until the mixture reaches a temperature of 70° to 80° C. and 25 ml. more of the dilute H_2SO_4 added. The excess permanganate is now titrated with N/5 $Na_2C_2O_4$, the oxalate being added slowly until the permanganate color is destroyed. Five ml. excess of the oxalate are added and the

exact excess determined by titrating the hot solution with N/5 $KMnO_4$ to a faint pink color. The total permanganate solution taken minus the oxalate titration = ml. $KMnO_4$ required by the nitrite.

Standard ferrous sulfate, $FeSO_4$, may be used, in place of sodium oxalate. The titration then may be conducted in the cold.

One ml. N/5 $KMnO_4$ = 0.0038 g. N_2O_3, or 0.0069 g. $NaNO_2$, or 0.0085 g. KNO_2.

Titration with Ceric Sulfate.—See chapter on Standard Solutions.

Detection of a Nitrate in a Nitrite Salt.—Iridium salts are colored blue by HNO_3 but no color is produced by HNO_2. Use a 0.025% solution of IrO_2 or $(NH_4)_2IrCl_6$ per 100 ml. of 98–99% H_2SO_4 and heat to boiling. The solution should be kept in a stoppered bottle. Into the hot reagent in a test tube is dropped the solid substance tested. A blue color is produced by nitrates. If the nitrite is in solution, make alkaline with KOH, evaporate to dryness and test the residue. Chlorine interferes, but not $FeCl_3$.

DETERMINATION OF PYRIDINE IN AMMONIUM NITRATE[23]

Dissolve 250 g. of sample in 300 ml. of distilled water, using a 1000-ml. Kjeldahl or Florence flask. Add a few drops of methyl orange and neutralize with 10% sodium hydroxide solution. Then add 15 ml. excess of 10% sodium hydroxide solution. Set up apparatus, note Fig. 74, using 300 ml. hypobromite solution in the second flask and receiving the distillate in 25 ml. N/10 sulfuric acid. Distil until 100 ml. of distillate have been collected. The heating should be very slow until all the ammonia, driven off, has been destroyed. This point will be indicated first by an acid reaction of the methyl orange in the first flask and second by the gradual reduction of the amount of nitrogen given off, in very small bubbles, in the hypobromite. At this point the hypobromite flask should not be warm enough to burn the hand (not above 70° to 75° C.). It is now safe to increase the heat so that boiling occurs in the hypobromite in 10 to 15 minutes and 100 ml. of distillate comes over in 20 to 25 minutes after active boiling starts.

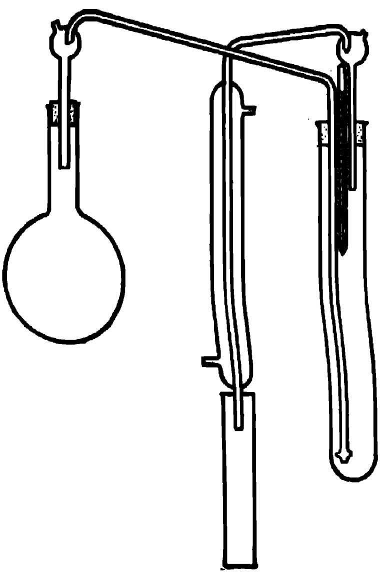


FIG. 74.—Apparatus for Pyridine.

The whole is set around a single ring stand. The hypobromite flask is 2 in. by 14 in. The hypobromite, 300 ml., occupies 7½ in. of the height at the start of the test.

Titrate the liquid in the receiver, using N/10 sodium hydroxide solution with methyl orange as the indicator.

Record the end-point; add ½ ml. of phenolphthalein (1 : 1000) solution and continue the titration until a red color which will persist for 30 seconds appears.

[23] R. M. Ladd, J. Ind. Eng. Chem., 11, 552, 1919.

Subtract the methyl orange end-point from that obtained with phenolphthalein, and multiply the difference by 0.0079. The result is the pyridine bases in grams. Methyl orange indicates pyridine plus ammonia. Phenolphthalein indicates ammonia. Difference is due to pyridine.

NOTES.—Because of the fact that the methyl orange and phenolphthalein end-points are never quite the same and because an absorption of carbon dioxide by the sodium hydroxide solution may bring it about that they vary still more widely, it is necessary to standardize the solutions used to both end-points and to make a correction for their normal difference. This correction should be checked by a new standardization at least once a week. We found that with our solutions this difference was usually about 0.4 ml.

In case it is desired to use a sample of a different size, maintain the proportions indicated above, except that the total solution in the first flask should always be about 500 ml.

The hypobromite solution is made up as follows: 100 g. sodium hydroxide are dissolved in 800 ml. of water, 25 ml. of liquid bromine are added, and the mixture shaken until the bromine is entirely dissolved and made up to 1000 ml. The solution should be made up a day in advance. It will maintain its strength for at least a week if kept in a stoppered, dark bottle. It will be brown in color. Should the brown color disappear during the distillation it would mean that an excess of ammonia is present. This should also be indicated and eliminated from the calculations by the double end-point called for, but in case this happens it is well to repeat the test, using more of the hypobromite solution.

The reactions involved and the calculations on which the proportions are based are indicated in the following equations:

$$\underset{40}{NaOH}+NH_4NO_3 \rightarrow \underset{17}{NH_3}+H_2O+NaNO_3.$$

15 ml. 10% sodium hydroxide solution contains 1.5 g. sodium hydroxide.
1.5 g. sodium hydroxide will free 0.6375 g. ammonia.

$$\underset{34}{2NH_3}+\underset{357}{3NaBrO} \rightarrow 3H_2O+N_2+3NaBr.$$

0.638 g. ammonia is destroyed by 6.699 g. sodium hypobromite.

$$\underset{80}{2NaOH}+\underset{160}{Br_2} \rightarrow \underset{119}{NaBrO}+NaBr+H_2O.$$

25 ml. bromine = 79.5 g. bromine.
300 ml. solution contains 17.7 g. hypobromite (approx.).

DETERMINATION OF NITROGEN IN STEEL[24]

For the determination of nitrogen in steel, a modification of the method first published by A. H. Allen and modified by Prof. J. W. Langley is used.

By the following method the sample and standard distillates are prepared under similar conditions, and when treated with Nessler reagent, develop

[24] Methods of Analysis used in Laboratories of the Titanium Alloy Manufacturing Co. Contributed by L. E. Barton.

colors nearly identical in quality or tone, but proportional in intensity to the ammonia present.

If the Nessler reagent is carefully prepared and works properly, the color in sample and standard will develop almost instantly and is fully developed in less than one minute. The solutions treated with such reagent remain clear or do not cloud appreciably on standing for ten minutes; however, the comparison is best made after standing one minute, and all difficulty due to clouding is avoided.

The difficulties of comparison are also reduced to a minimum by using an aliquot part of the distillate in the manner to be described instead of that corresponding to the whole sample.

Preparation of Reagents.—Hydrochloric acid of 1.1 sp.gr., free from ammonia, which may be prepared by distilling pure hydrochloric acid gas into distilled water free from ammonia. To do this, take a large flask fitted with a rubber stopper carrying a separatory funnel-tube and an evolution-tube, fill it half full of strong hydrochloric acid, connect the evolution-tube with a wash-bottle connected with a bottle containing the distilled water. Admit conc. sulfuric acid free from nitrous acid to the flask through the funnel-tube, apply heat as required, and distill the gas into the prepared water.

Test the acid by admitting some of it into the distilling apparatus, described farther on, and distilling it from an excess of pure caustic soda, or determine the amount of ammonia in a portion of hydrochloric acid of 1.1 sp.gr., and use the amount found as a correction.

NOTE.—The ammonia-free hydrochloric acid may also be prepared as follows:

Dilute concentrated hydrochloric acid to specific gravity 1.10 and without addition of sulfuric acid distill it.

Hydrochloric acid of this strength distills without change in concentration.

The first 100-ml. distillate from one litre of acid will usually contain all the ammonia and is rejected; the portions distilled thereafter being collected for use but must, of course, be tested as usual to make sure it is free from ammonia.

Solution of caustic soda, made by dissolving 300 grams of fused caustic soda in 500 ml. of water and digesting it for 24 hours at 50° C. on a copper zinc couple, made, as described by Gladstone and Tribe, as follows:

Place from 25 to 30 grams of thin sheet zinc in a flask and cover with a moderately concentrated, slightly warm solution of copper sulfate. A thick, spongy coating of copper will be deposited on the zinc. Pour off the solution in about ten minutes and wash thoroughly with cold distilled water.

Nessler Reagent.—Dissolve 35 grams of potassium iodide in a small quantity of distilled water, and add a strong solution of mercuric chloride little by little, shaking after each addition until the red precipitate formed dissolves. Finally the precipitate formed will fail to dissolve, then stop the addition of the mercury salt and filter. Add to the filtrate 120 grams of caustic soda dissolved in a small amount of water, and dilute until the entire solution measures 1 liter. Add to this 5 ml. of saturated aqueous solution of mercuric chloride, mix thoroughly, allow the precipitate formed to settle, and decant or siphon off the clear liquid into a glass-stoppered bottle.

Standard Ammonia Solution.—Dissolve 0.0382 gram of ammonium chloride in 1 liter of water. One ml. of this solution will equal 0.01 milligram of nitrogen.

Distilled Water Free From Ammonia.—If the ordinary distilled water contains ammonia, redistill it, reject the first portions coming over, and use the subsequent portions, which will be found free from ammonia. Several glass cylinders of colorless glass of about 160 ml. capacity are also required.

The best form of distilling apparatus consists of an Erlenmeyer flask of about 1500 ml. capacity, with a rubber stopper, carrying a separatory funnel-tube and an evolution-tube, the latter connected with a condensing-tube around which passes a constant stream of cold water. The inside tube, where it issues from the condenser

should be sufficiently high to dip into one of the glass cylinders placed on the working table.

METHOD OF DETERMINATION

Distillation of Sample

In a distilling flask of 1000 to 1500 ml. capacity, fitted with separatory funnel and connected with condenser, place 40 ml. prepared caustic soda solution; add 500 ml. distilled water and distill until the distillate gives no reaction with Nessler reagent.

Dissolve a 5-gram sample of the steel in 40 ml. of ammonia-free hydrochloric acid, and by means of the separatory funnel add the solution slowly to the contents of the distilling flask, washing in finally with ammonia-free water.

Distill and collect 150 ml. of distillate in a graduated flask. Cork the flask and set aside. Experience has shown that 150 ml. of distillate will contain all the nitrogen in the sample.

PREPARATION OF STANDARD

After distilling the sample—the apparatus then being free from ammonia but containing the residue of sample and reagents—25 ml. of standard ammonium chloride solution and 150 ml. of ammonia-free water are added to the contents of the flask, and distillation continued until a *standard* distillate of 150 ml. is collected in a graduated flask.

As before, the single distillate will contain all the ammonia from 25 ml. of standard solution.

To the standard distillate is added 6 ml. of Nessler reagent; and since the standard ammonium chloride solution is equivalent to .00001 g. nitrogen per ml., 1 ml. prepared standard distillate is equivalent to $\frac{25 \times .00001}{156} = .0000016$ g., nitrogen per ml. $= .00016\%$ nitrogen when using one gram sample.

COMPARISON AND DETERMINATION

To make the determination, 30 ml. of *sample distillate*, equal to *one gram* of sample, are placed in one of a pair of Nessler jars and the color developed by addition of 1 ml. Nessler reagent.

The standard and sample are allowed to stand one minute to fully develop the color.

Into the other jar the standard distillate is run from a burette until the colors in standard and sample jars are of the same intensity; the final comparison being made after bringing the contents of the jars to the same volume by addition of ammonia-free water to one or the other.

The number of ml. of standard distillate multiplied by .00016 gives the percentage of nitrogen in the steel.

DETERMINATION OF CONVERTER EFFICIENCY IN OXIDATION OF AMMONIA TO NITRIC ACID

In place of determining the total ammonia used and the total products of *oxidation, samples may be taken, during the operation, of gases entering and leaving the converter and analyzed according to the following simple and accurate procedure suggested by Gaillard;*[25] *a method successfully used by the* American Cyanamide Company at Warners, N. J., and by the United States nitrate plants at Sheffield and Muscle Shoals, Ala.

Principle.—The gas to be analyzed is drawn into an evacuated bulb which has previously been weighed, and the increased weight due to the sample is obtained. The ammonia or nitrogen oxides in the bulb are then absorbed and titrated, and the percentage by weight of combined nitrogen in the gases is determined. The efficiency is the ratio of the combined nitrogen in the exit and inlet gases.

Sources of Error.—Error may be caused by:

(*a*) Water condensation in the sampling tube during sampling.

(*b*) Air leakage into the tube during sampling.

(*c*) Ammonia escaping oxidation being drawn into the bulb. In presence of ammonia a cloudiness is readily observed.

(*d*) Changes in temperature, barometric pressure, and moisture conditions between successive weighings of the same bulb.

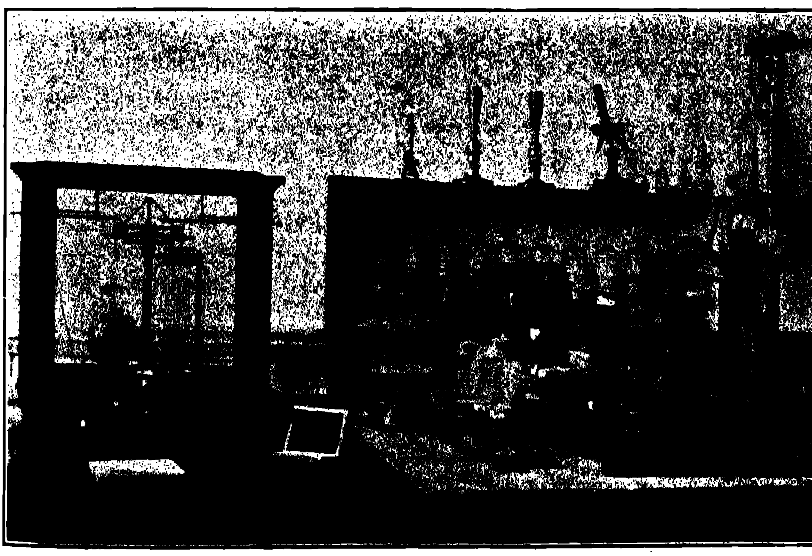


Fig. 75.—Evacuation and Weighing of Bulbs for Converter Efficiency in Ammonia Oxidation.

These errors are rendered negligible by careful manipulation. It is recommended that a similar bulb tare weight be used and the procedure for weighing recommended in combustion carbon determinations be followed.

[25] J. Ind. Eng. Chem., 11, 745, 1919.

On the right hand side of the illustration below is shown the bulb in the process of evacuation by means of a vacuum pump operated by an electric motor. Attached to the system is a mercury gauge or barometer which gives the degree of evacuation of the bulb.

On the left hand side of the illustration is shown a balance with a bulb suspended for weighing after being evacuated. It is advisable to have a bulb on the right hand arm of the balance acting as a tare weight. This counteracts the buoyancy error of the air, increasing the delicacy of weighing. If the stopcocks are not absolutely tight, the bulb will gain in weight owing to an intake of air.

CYANOGEN

DETECTION

Traces of Hydrocyanic Acid.—To the solution to be tested are added two drops of 10% NaOH and the mixture is evaporated nearly to dryness. After cooling, a drop of 2% ferrous sulfate is added and the sample allowed to stand in the cold for about fifteen minutes. Now 2–3 drops of conc. HCl are added and the solution warmed gently, then cooled. The solution is a blue green if HCN was present in the original sample. 0.000002 g. HCN may be detected.

NOTE.—Test for Cyanide. This depends upon the solvent action of HCN upon freshly precipitated HgO in presence of KOH. The filtrate is tested for mercury in an acid solution by addition of H_2S. (Hood.)

VOLUMETRIC DETERMINATION OF HYDROCYANIC ACID [26]

The method depends upon the decolorization of the blue ammoniacal solutions of cupric salts by a soluble cyanide, the reduction to cuprous condition making possible for an accurate quantitative estimation of the cyanide.

Standard Copper Sulfate.—Twenty-five grams of copper sulfate, $CuSO_4 \cdot 5H_2O$ are dissolved in a 1000-ml. flask with 500 ml. of distilled water and

[26] J. McDowell, Chem. News, 89, 229 (1904).

ammonium hydroxide added until the precipitate that first forms dissolves and a deep blue solution is obtained. Water is now added to make the volume exactly 1000 ml. The cupric solution is standardized by running a portion into a solution containing 0.5 gram pure potassium cyanide, KCN, per 100 ml. of water and 5 ml. of ammonium hydroxide until a faint blue color is evident. Chlorides do not interfere.

Procedure.—0.5 gram of the soluble cyanide is dissolved in 100 ml. of water and 5 ml. conc. ammonium hydroxide added. The standard cupric sulfate solution is now added until the blue color is obtained. The ml. required multiplied by the factor of the copper salt in terms of the salt sought gives the weight of that salt in the sample.

LIEBIG'S METHOD FOR DETERMINATION OF HYDROCYANIC ACID. SOLUBLE CYANIDES[27]

Silver nitrate reacts with an alkali cyanide in neutral or alkaline solution as follows: $AgNO_3+2KCN=Ag(CN)_2K+KNO_3$. The potassium silver cyanide is soluble, hence the precipitate that first forms immediately dissolves on stirring as long as the cyanide is present in excess or in sufficient quantity to react according to the equation. A drop of the silver salt in excess will produce a permanent turbidity, owing to the following reaction:

$Ag(CN)_2K+AgNO_3=2AgCN+KNO_3$, the insoluble AgCN being formed.

Procedure.—The alkali cyanide contained in a beaker placed over a sheet of black glazed paper, is treated with 4 to 5 ml. of 10% KOH solution and diluted to 100 ml. The liquid is now titrated with standard silver nitrate, with constant stirring, until a faint permanent turbidity is obtained.

One ml. N/10 $AgNO_3$ = 0.013023 gram KCN.

DETERMINATION OF CYANIDE BY VOLHARD'S METHOD

The method involves Volhard's method for determining halogens, the procedure depending upon the fact that the silver salts of cyanides are insoluble in dilute cold nitric acid solutions.

The neutral cyanide solution is treated with an excess of silver nitrate reagent, slightly acidified with nitric acid, and diluted to a definite volume in a measuring flask. A portion of the solution is now filtered through a dry filter, and a convenient aliquot portion of this is titrated with standard thiocyanate solution, using ferric alum as indicator (see page 668) to determine the silver nitrate present. From this calculate the excess silver nitrate reagent added and ascertain that combined with the cyanide.

One ml. N/10 $AgNO_3$ = 0.006511 g. KCN or 0.002602 g. CN.

DETERMINATION OF CYANIDE AND THIOCYANATE IN PRESENCE OF ONE ANOTHER

The cyanide is determined preferably by Liebig's method (above), and the ml. of $AgNO_3$ required recorded. To the alkaline or neutral solution is

[27] Ann. Chem. und Pharm., 77, 102 (1851).

662

COMPLEX COMPOUNDS—FERRO AND FERRI CYANIDES

HYDROFERROCYANIC ACID

One gram of the hydroferrocyanide in 100 ml. of water acidified with 10 ml. of sulfuric acid is titrated in a casserole with standard potassium permanganate to a permanent pink color. The end-point is poor, so that it is advisable to standardize the permanganate against pure potassium ferrocyanide.

Reaction: $2H_4Fe(CN)_6 + O = H_2O + 2K_3Fe(CN)_6$.

One ml. N $KMnO_4 = 0.3683$ gram $K_4Fe(CN)_6$.

HYDROFERRICYANIC ACID

Ten grams of hydroferricyanide are dissolved in water, the solution made alkaline with KOH and heated to boiling and an excess of ferrous sulfate solution added. The yellowish brown ferric hydroxide turns black with excess of ferrous salt. The solution is diluted to exactly 500 ml. and 50 ml. of a filtered portion titrated with potassium permangate.

One ml. N $KMnO_4 = .3292$ gram $K_3Fe(CN)_6$.

CYANAMID [29]

1. Sampling

The sample shall consist of at least two pounds of the material taken from every other bag composing the lot or shipment, by means of a tube which shall remove a core from the top to the bottom of the container. Pass all through a 48 mesh Tyler screen, grinding any oversize if necessary. Mix the portions thoroughly by rolling on a clean oil cloth or paper and quarter until the desired amount is obtained. Place the final sample in two containers and seal airtight. One is for analysis, and one for referee.

2. Nitrogen

Determine the total nitrogen according to the Official Gunning Method described in the text. Report the nitrogen found, as ammonia (NH_3).

3. Calcium Carbide

Determine by weighing a convenient quantity of the material and transferring to an apparatus equipped to measure the volume of acetylene liberated by addition of water to the sample.

4. Oil

Weigh a two (2) gram portion into the thimble of a Soxhlet apparatus and extract the oil with carbon tetrachloride. Collect the extract in a weighed flask and evaporate off the carbon tetrachloride on a water bath. Complete the

[29] Courtesy of American Cyanamid Co.

removal of the solvent by heating 15 minutes in a drying oven at 105° C. Weigh and calculate the percentage of oil.

AERO BRAND CYANIDE [30]

1. Sampling

Ten (10) drums in each lot of 4000 lbs. shall be sampled. The portions removed shall have a combined weight of approximately one (1) pound. The sample shall be taken as soon as the drum is filled, by inserting a long sampling rod or tryer the full depth of the drum and depositing the sample in a suitable container.

A portion of the sample is removed at the laboratory for analysis and the container is sealed air tight and retained for six months as a reference sample.

2. Total Cyanide Content

A. Reagents. *1. Standard Silver Nitrate Solution.*—Dissolve seventeen (17) grams of silver nitrate in 200 ml. of distilled water, filter, and dilute to one liter.

2. Soda-Lead Mixture.—Dissolve 200 grams of anhydrous sodium carbonate in 700 ml. of distilled water and filter. Dissolve twenty (20) grams of lead acetate ($Pb(CH_3CO_2)_2 \cdot 3H_2O$) in 200 grams of distilled water, filter and add the filtrate to the solution of sodium carbonate. Dilute to one liter. Shake the solution well each time before using.

3. Alkaline Iodide Indicator.—Dissolve thirty (30) grams of potassium iodide in one (1) liter of ten (10) % sodium hydroxide solution.

B. Standardization of Reagents. *1. Standard Silver Nitrate Solution.*—Standardize the solution against an accurately weighed sample of pure sodium chloride, previously dried for one (1) hour at 105° C., using potassium chromate indicator.[31]

C. Determination.—Place 200 ml. of distilled water in a 500 ml. volumetric flask and carefully dry the neck of the flask. Weigh rapidly and accurately a five (5) gram sample of the flake cyanide or "Cyanogas" and transfer it to the flask. Wash down the sides of the flask and thoroughly mix the sample with a whirling motion. Agitate the solution at intervals for fifteen (15) minutes, then add thirty (30) ml. of the soda-lead mixture, mixing the latter well before measuring it. Thereafter agitate the solution every five (5) minutes for one-half (0.5) hour. Then make the solution up to volume, mix thoroughly, and filter through a dry filter paper into a dry beaker. Reject the first twenty-five (25) ml. of filtrate, rinsing the beaker with the rejected portion. Now continue filtration, collecting at least 150 ml. of filtrate. Measure out 100 ml. with a calibrated pipette, place in an 800 ml. beaker, dilute to 400 ml., and add five (5) ml. of the alkaline iodide indicator. Titrate with the standard silver nitrate solution until a faint blue opalescence shows permanently against a black background. Calculate the % calcium cyanide in the sample.

$$1.0 \text{ ml. } 0.1 \text{ N } AgNO_3 = 0.00921 \text{ gms. } Ca(CN)_2.$$

[30] By courtesy of American Cyanamid Co.
[31] See page 667.

3. Total Sulfur

Weigh accurately two (2) grams of the flake cyanide and transfer to a 400-ml. beaker containing fifty (50) ml. of distilled water. Add twenty-five (25) ml. of a saturated solution of bromine in concentrated nitric acid. Stir the mixture for five (5) minutes and then boil down to dryness. Moisten the residue thoroughly with concentrated hydrochloric acid and evaporate to dryness again. Add ten (10) ml. of concentrated hydrochloric acid and then 150 ml. of water boil, filter and wash thoroughly. Heat the filtrate to 90° C. and add with constant stirring five (5) ml. of ten (10) % solution of barium chloride. After digesting the solution at 90° C. for one (1) hour on a water bath, filter the barium sulfate through an ashless filter paper, and wash the precipitate thoroughly with hot (80° C.) distilled water. Transfer the filter paper containing the precipitate to a weighed platinum crucible, and ignite in a muffle with free access of air. Cool and weigh the barium sulfate and calculate the per cent of sulfur in the sample.

HYDROCYANIC ACID [32]

1. Sampling

Each official sample for analysis shall consist of at least one (1) pound of material taken in the following manner: During the filling of the first cylinder, the last and one or more intermediate cylinders depending on the number composing the shipment, draw off through a by-pass in the filling line, about twenty-five (25) ml. of the liquid into an iced container. After all the samples have been taken, close the container and agitate gently to secure the proper mixing of the contents. All of the succeeding determinations are to be made in open air, not in a laboratory, after which the sample may be disposed of in any suitable manner.

2. Total Hydrocyanic Acid

Place a portion of the sample in an iced hydrometer jar, determine the specific gravity by means of a calibrated hydrometer and note the temperature of the liquid. Determine the hydrocyanic acid content from the specific gravity—composition table given in Bulletin No. 308, University of California Experiment Station (reproduced in Van Nostrand's Chemical Annual).

3. Total Acidity

Dilute a fifty (50) ml. portion of the sample with 300 ml. of distilled water. Add three (3) drops of one (1) % methyl red indicator and titrate until nearly colorless with one-tenth (0.1) normal sodium hydroxide solution. Add two drops more of the indicator and titrate to the appearance of a yellow color. Calculate the acidity in terms of sulfuric acid.

SODIUM FERROCYANIDE [33]

1. Sampling

Each official sample sent to the laboratory shall consist of at least two (2) pounds of material taken in the following manner: Take approximately one-half

[32] By courtesy of American Cyanamid Co.
[33] By courtesy of American Cyanamid Co.

(0.5) pound of the crystals from a few inches below the surface of every third barrel comprising the lot or shipment. Thoroughly mix the several portions together on a clean oil cloth or paper, reduce by quartering to the quantity of sample required, and place in an air-tight container.

2. Moisture

Heat twenty (20) grams of the crystals for six hours at 105° C. Cool in a desiccator and weigh. Grind this dried sample rapidly in a mortar. Heat three (3) grams of the powder to constant weight at 105° C. Calculate the total water content and subtract from it the water of crystallization equivalent to the sodium ferrocyanide content of the sample as determined in (3) and calculate to $Na_4Fe(CN)_610\ H_2O$. The difference is the free moisture in the sample.

3. Total Sodium Ferrocyanide

A. Reagents. *1. Standard Potassium Permanganate Solution.*—Dissolve three and two-tenths (3.2) grams of potassium permanganate in 500 ml. of distilled water. Place the solution in a stoppered bottle and allow it to stand in the dark for two (2) days. Filter the solution through a Gooch crucible, using an asbestos mat, and dilute the filtrate to one (1) liter.

2. Standard Potassium Ferrocyanide Solution.—Dissolve forty-two (42) grams of pure potassium ferrocyanide, $K_4\ Fe(CN)_6\ 3H_2O$ in 500 ml. of distilled water, filter, and dilute the filtrate to one (1) liter.

3. Standard Zinc Chloride Solution.—Dissolve ten (10) grams of pure zinc in a mixture of 150 ml. of concentrated hydrochloric acid and 300 ml. of distilled water. Dissolve 200 grams of ammonium chloride in the zinc chloride solution, filter, and dilute the filtrate to one (1) liter.

4. Potassium Chloride Solution.—Dissolve 100 grams of pure potassium chloride in 600 ml. of distilled water, filter, and dilute the filtrate to one (1) liter.

5. Uranium Nitrate Indicator.—Dissolve three (3) grams of uranyl nitrate $UO_2\cdot(NO_3)_2\cdot 6H_2O$ in fifty (50) ml. of distilled water.

B. Standardization of Reagents. *1. Standard Potassium Permanganate Solution.*—Dissolve one-quarter (0.25) of a gram of pure sodium oxalate ($Na_2C_2O_4$) obtained from the U. S. Bureau of Standards, in 175 ml. of distilled water, and add twenty-five (25) ml. of dilute sulfuric acid (one to four). Heat the solution to 80° C. and titrate with the standard potassium permanganate solution until the solution assumes a faint pink color.

2. Standard Potassium Ferrocyanide Solution.—Measure out twenty-five (25) ml. of solution, dilute to 500 ml. and add five (5) ml. of concentrated sulfuric acid. Titrate with the standard potassium permanganate solution until the solution assumes a faint pink color. Calculate the quantity of sodium ferrocyanide $Na_4Fe\ (CN)_6\cdot 10H_2O$ equivalent to one (1) ml. of the potassium ferrocyanide solution.

$$\text{One ml. } 0.1\ N\ K_4Fe(CN)_6 = 0.4841\ \text{gm. } Na_4Fe\ (CN)_6\cdot 10\ H_2O.$$

3. Standard Zinc Chloride Solution.—Measure out twenty-five (25) ml. of solution with a calibrated burette, add ten (10) ml. of ten (10) % potassium chloride solution and dilute to 200 ml. Heat the solution to 90° C. (do not boil

the solution) and titrate with the standard potassium ferrocyanide solution until a drop of uranyl nitrate solution, used on a spot plate as an outside indicator, turns faintly brown. Add the ferrocyanide solution rapidly with constant stirring until near the end-point (within 1 to 4 ml.) The zinc chloride solution is blue at first, but turns almost white at the end-point. When near the end-point, add the ferrocyanide solution in one-half (0.5) ml. portions, and stir for at least fifteen (15) seconds before testing with the indicator. When the end-point has been passed, add one-half (0.5) ml. of standard zinc chloride solution, and again titrate with the standard potassium ferrocyanide solution, testing the solution with the indicator after the addition of each drop of the ferrocyanide solution. Make a check determination. Calculate the amount of the potassium ferrocyanide solution exactly equivalent to twenty-five (25) ml. of the zinc chloride solution.

C. Determination.—Weigh accurately a thirty (30) gram sample of sodium ferrocyanide, dissolve in distilled water and dilute to one liter. Measure accurately twenty-five (25) ml. of the standard zinc chloride into a 400-ml. beaker, add ten (10) ml. of the ten (10) % potassium chloride solution and one hundred and sixty-five (165) ml. of distilled water. Heat the solution to 90° C. (do not boil the solution) and titrate with constant stirring with the sodium ferrocyanide solution using uranyl nitrate as an outside indicator, following the procedure given for the standardization of the zinc chloride solution (3 **B** *3*).

The value of the zinc chloride solution has been determined in terms of sodium ferrocyanide. From this value calculate the sodium ferrocyanide $Na_4Fe(CN)_6 \cdot 10\ H_2O$ present in the sample.

4. Total Sodium Chloride

A. Reagents. *1. Standard Silver Nitrate Solution.*—Dissolve eight and one-half (8.5) grams of silver nitrate in water, filter and dilute the filtrate to one (1) liter.

2. Standard Ammonium Thiocyanate Solution.—Dissolve three and eight-tenths (3.8) grams of ammonium thiocyanate in approximately 100 ml. of water, filter, and dilute to one (1) liter.

3. Zinc Nitrate Solution.—Dissolve 100 grams of zinc nitrate in 500 ml. of distilled water, filter, and dilute to one (1) liter.

4. Ferric Ammonium Sulfate Solution.—Saturate 100 ml. of distilled water with ferric ammonium sulfate, at room temperature (20° C.). Filter, and add just enough nitric acid to remove the turbidity and to change the color from red to pale yellow.

5. Potassium Chromate Solution.—Prepare a saturated solution of the C.P. salt in distilled water.

B. Standardization of Reagents. *1. Standard Silver Nitrate Solution.*—Weight accurately two-tenths (0.20) of a gram of pure sodium chloride, previously dried at 105° C. for one (1) hour, and dissolve it in 50 ml. of distilled water. Add two (2) drops of potassium chromate indicator and titrate with the silver nitrate solution to the appearance of a brown coloration. Calculate the amount of silver nitrate equivalent to the sodium chloride and then calculate the normality of the standard solution.

2. Standard Ammonium Thiocyanate Solution.—Measure accurately from a burette, thirty-five (35) ml. of the standard silver nitrate solution, add 2 ml. of concentrated nitric acid, and dilute to 150 ml. with distilled water. Titrate with the ammonium thiocyanate solution, using one (1) ml. of the ferric ammonium sulfate indicator. Calculate the volume of the ammonium thiocyanate solution equivalent to one (1) ml. of the standard silver nitrate solution.

C. Determination.—Heat 100 ml. of the sample solution (*3*C) to 80° C. and add with constant stirring fifty (50) ml. of a hot (80° C.) ten (10) % solution of zinc nitrate, to precipitate the ferrocyanide as zinc ferrocyanide. Filter and wash the precipitate. To the filtrate add two (2) ml. of concentrated nitric acid and fifteen (15) ml. of standard silver nitrate solution. Filter and wash the precipitate. Titrate the excess silver nitrate with the standard ammonium thiocyanate solution, using the ferric ammonium sulfate indicator, and calculate the % sodium chloride in the sample.

5. Total Sodium Sulfate

A. Reagents. *1. Zinc Chloride Solution.*—Dissolve 100 grams of zinc chloride in 500 ml. of distilled water, filter and dilute to one (1) liter.

2. Barium Chloride Solution.—Dissolve 100 grams of barium chloride ($BaCl_2 \cdot 2H_2O$) in 500 ml. of distilled water, filter, and dilute to one (1) liter.

B. Determination.—Heat 100 ml. of the sample solution (*3*C) to 80° C. and add with constant stirring fifty (50) ml. of a hot (80° C.) ten (10) % solution of zinc chloride, to precipitate the ferrocyanide as zinc ferrocyanide. Filter and wash the precipitate. Acidify the filtrate with concentrated hydrochloric acid and then add two (2) ml. in excess. Heat the solution to boiling, add with constant stirring fifteen (15) ml. of the ten (10) % barium chloride solution, and digest at 90° C. for two (2) hours. Filter the precipitate through an ashless filter, wash with two (2) % hydrochloric acid until the residue is white, and then follow with successive portions of hot (60° C.) water until the filtrate is free from chloride by the silver nitrate test. Place the filter and the precipitate in a platinum crucible and ignite for one-half (0.5) an hour in a muffle with free access of air. Cool the crucible in a desiccator, weigh, and report the per cent of sodium sulfate.

6. Foreign Matter

Dissolve fifty (50) grams of the material in 300 ml. of hot water and filter off the insoluble matter on a weighed Gooch crucible. Wash the residue thoroughly with hot water. Dry the crucible in an oven at 105° C. and weigh. Calculate the per cent of insoluble or foreign matter.

OXYGEN

O, *at.wt.* 16.00; *b.p.* −182° C.; *wt. per l.* 1.429 g. (liquid, *sp.gr.* 1.12)

Oxygen[1] is a colorless, tasteless, odorless gas. It is found free in the atmosphere to the extent of about 21% by volume. Combined with hydrogen it is a constituent of water (88.8% by weight). It is an exceedingly active element and combines with all elements except fluorine. It is a constituent of a great number of minerals and an important constituent of animal and vegetable matter. About half our globe is oxygen, combined or free.

DETECTION

Free oxygen is recognized by its activity in combining with substances when heated. A lighted taper plunged into oxygen gas burns brilliantly. The burning of the taper in the air is due to oxygen.

Hydrogen passed over a highly heated oxide, in a majority of simple compounds, combines with it forming water.

Certain oxides and salts heated decompose giving off oxygen, for example 2HgO decomposes to 2Hg and O_2, $2KClO_3$ to 2KCl and $3O_2$.

Carbon combines with oxygen at kindling temperature forming CO_2, a gas detected by means of lime water. (See chapter on Carbon.)

ESTIMATION

The determination of oxygen in a gas mixture is accomplished by the combination and subsequent absorption of oxygen, the gas contraction being due to oxygen. Pyrogallic acid or phosphorus are commonly used for this purpose. (See chapter on Gas Analysis.)

The determination of combined oxygen is difficult and seldom attempted. It is frequently estimated by difference after determining the other constituents of the substance, after definitely establishing the presence of oxygen.

[1] Priestley, Scheele and Lavoisier are generally credited with the discovery and isolation of oxygen. Lavoisier named the element oxygen (1777)—acid producer—from his erroneous belief that it was a constituent of all acids.

Typical examples of the determination of free and combined oxygen will be considered here. For further consideration of the element in gaseous mixtures see the chapter on Gas Analysis in Volume II.

INSTRUCTIONS FOR THE ANALYSIS OF COMMERCIAL OXYGEN[2]

Theory.—A method for the determination of oxygen in gas mixtures containing from 95 to 100% oxygen is based on the fact that clean bright copper oxidizes rapidly in the presence of ammonia vapor. The oxide that is formed is dissolved by a saturated solution of ammonium chloride, thus exposing fresh copper to the remaining gas.

Apparatus.—The apparatus for the determination of oxygen in commercial oxygen is shown assembled in Fig. 76, "Apparatus for Determination of Oxygen in Commercial Oxygen." The various units making up this assembly are designated by letters (see table, p. 671) and these will be used in identifying the pieces of equipment in this description.

The sample is measured in burette *A* and transferred through the transparent tubing *S* and the connecting tube *E* to the absorption pipette *B*. The displaced pipette solution passes into the storage pipette *C* by means of the tee tube *D*.

The aspirator bottle *F* is connected to the burette *A* by means of about 42 inches of rubber tubing *J*. The aspirator bottle and the burette both contain distilled water and transference of the gas sample from the burette to the pipette is accomplished by raising and lowering of the aspirator bottle.

The Bakelite support *T* is used to adjust the level of the copper coils in *B* and is held in position by friction on the sides of the hole in rubber stopper *V*. Clip *M* is used to hold this stopper in position.

The glassware is mounted on a metal frame *L* by means of the clamps *R*, *P* and *N*. This frame is secured to a base *K* and the whole structure keyed to the shaft of a pendulum shaking apparatus.

Preparation of Solutions.—The absorption liquid for use in the pipette *B* consists of a solution of equal volumes of ammonium hydroxide (NH_4OH) and distilled water, saturated with ammonium chloride (NH_4Cl).

The *ammonium hydroxide* shall be of C.P. grade of 0.90 specific gravity. The *ammonium chloride* (sal ammoniac, or muriate of ammonia) should be of the grade technically known as white ammonium chloride. *Water* used in the preparation of the pipette solution and in the burette should be *distilled water*. Electrically "purified" and other special waters still contain impurities that might introduce errors in the results obtained and therefore must not be used.

Procedure.—Measure out six quarts of distilled water and pour it into a clean 5-gallon bottle. Measure out six quarts of ammonium hydroxide (NH_4OH) and add it to the distilled water in the 5-gallon bottle. Weigh out nine pounds of ammonium chloride and add it to the solution of water and ammonium hydroxide in the 5-gallon bottle.

Stopper the 5-gallon bottle containing the mixture with a rubber stopper and agitate by shaking the bottle every ten minutes for a period of two hours. Allow the bottle and its contents to stand for a period of eight hours. Pour off

[2] Standard method of the Linde Air Products Company, by courtesy of that company.

List of Parts.

Part	Number required	Description
A	1	100 ml. oxygen burette
B	1	Absorption pipette
C	1	Storage pipette
D	1	Glass tee tube
E	1	Glass connection tube
F	1	Aspirator bottle, 250 ml.
G	1	No. 10 rubber stopper
H	1	Mohr pinchcock clamp, small size
J	–	5/16″ outer diameter rubber tubing
K	1	Base for rocking pipette stand
L	1	Rocking pipette stand
M	1	Clip for absorption pipette stopper
N	1	Clamp with wing nuts
P	2	Clamps with wing nuts
Q	1	7/16″ steel rod, 16½″ long
R	2	Burette clamps
S	–	Transparent rubber tubing of 5 mm. bore, 1¾ mm. wall
T	1	Bakelite support
V	1	No. 10 rubber stopper

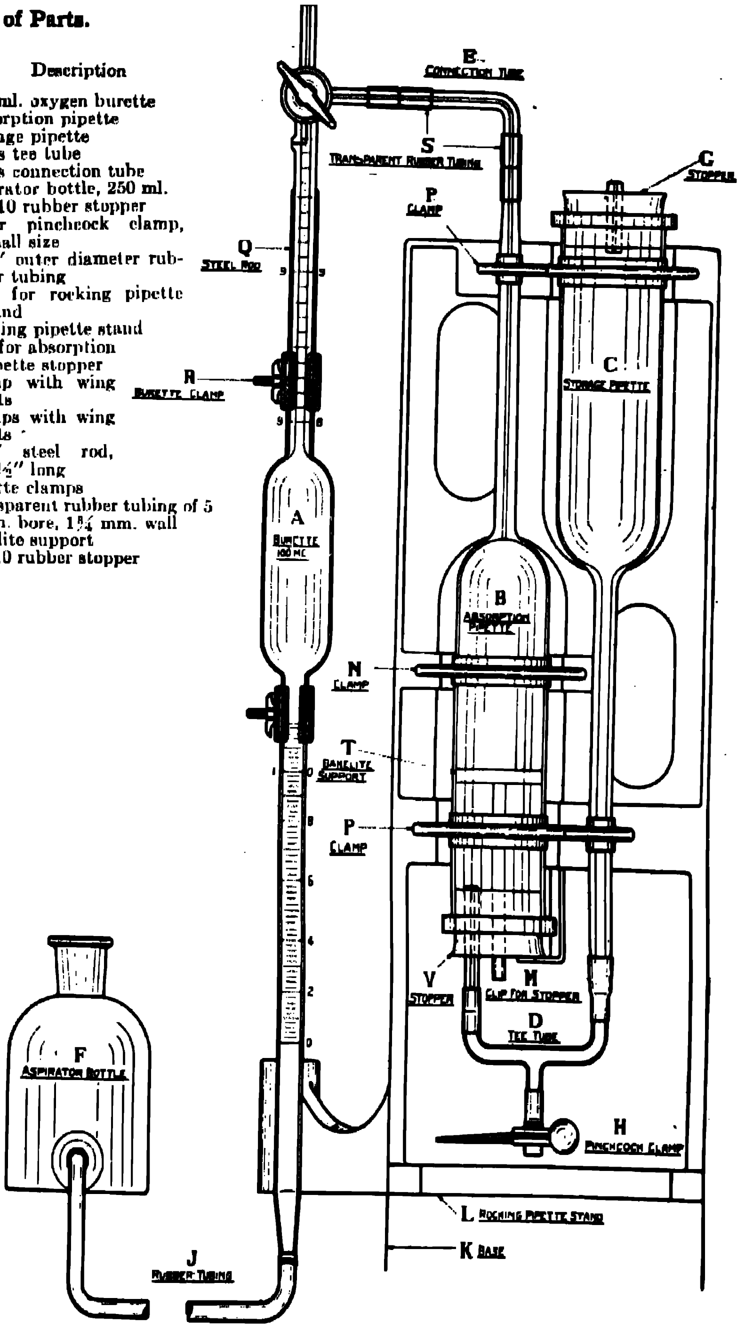
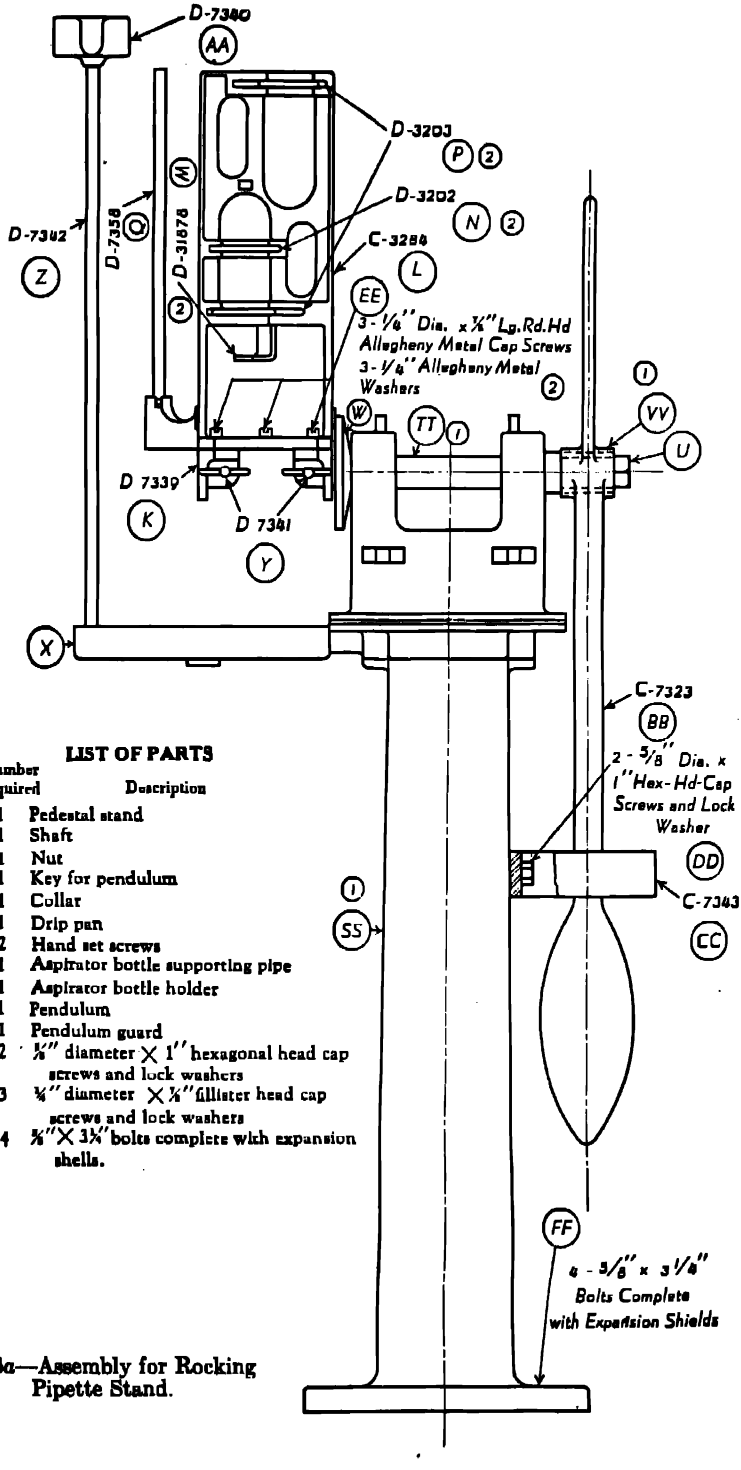


FIG. 76.—Apparatus for the Determination of O_2 in Commercial O_2.



LIST OF PARTS

Part	Number required	Description
SS	1	Pedestal stand
TT	1	Shaft
U	1	Nut
VV	1	Key for pendulum
W	1	Collar
X	1	Drip pan
Y	2	Hand set screws
Z	1	Aspirator bottle supporting pipe
AA	1	Aspirator bottle holder
BB	1	Pendulum
CC	1	Pendulum guard
DD	2	⅝" diameter × 1" hexagonal head cap screws and lock washers
EE	3	¼" diameter × ⅜" fillister head cap screws and lock washers
FF	4	⅝" × 3¼" bolts complete with expansion shells.

Fig. 76a—Assembly for Rocking Pipette Stand.

the quantity of solution required for immediate use, being careful not to stir up the material that has settled to the bottom. Restopper the 5-gallon bottle with a rubber stopper and store it in a cool place.

Distilled water is used as the burette liquid.

Preparation of Apparatus for Test.—Prepare copper spirals by winding about two feet of clean No. 20 copper wire on a rod ¼ inch in diameter. Fill pipette *B* with the spirals to within one inch of the opening for the stopper *V*. Insert the Bakelite support *T* through the hole in the center of the rubber stopper *V* and place the stopper in the position shown in Fig. 76. Adjust the Bakelite support until the copper spirals reach to about ¼ inch from the top of the pipette.

Install the pipettes and the burette on the metal frame and make all connections as shown in Fig. 76. Grease the three-way stopcock on the burette *A*, applying the stopcock grease sparingly so as to avoid plugging the passages. Remove the rubber stopper *G* from the pipette *C*; close off the pipettes by means of the three-way stopcock on burette *A*. Fill the pipette *C* with ammonium chloride pipette solution. Replace stopper *G* and open the pipettes to the air by turning the stopcock on *A*. The pipette liquid should then stand above the constrictions in both pipettes.

Connect the aspirator bottle *F* to the burette *A* by means of 42 inches of tubing *J*, and fill the bottle with 150 ml. of distilled water. Turn the burette stopcock so that the burette and the pipette are connected, and draw over into the burette any gas in the pipette by lowering the aspirator bottle. Turn the stopcock to open the burette to the air, and, by raising the aspirator bottle, force out this gas, at the same time filling the burette with water from the aspirator bottle until it flows from the short tube above the stopcock, which hereafter will be called the *sampling connection.*

"Season" the pipette solution by transferring five samples of approximately 100 ml. each of commercial oxygen from the burette to the pipette. Shake for three minutes and then draw the residual gases back into the burette as before. Open the burette to the air and by raising the aspirator bottle force the gas out of the burette until the water from the bottle flows out of the sampling connection. Close the stopcock and the apparatus is ready for accurate testing.

Method of Test.—Purge the sampling hose and the source of supply by starting a flow of gas through the rubber hose connected to this source. Attach the rubber tubing to the sampling connection, open the stopcock quickly to permit the oxygen to flow into the burette only. Take a sample of slightly over 100 ml. before closing the stopcock. Allow 15 seconds for the water to drain down the walls of the burette; then adjust the volume of the gas to exactly 100 ml. by holding the aspirator bottle so that its liquid level is on a line with the zero graduation of the burette, gradually opening the stopcock to the atmosphere, discharging the excess gas until the meniscus of the liquid is also even with the zero mark. Close the stopcock immediately to prevent too much sample being discharged or air being drawn in. Turn the stopcock so as to connect the burette with the pipette and, by raising the aspirator bottle, pass the entire sample over into the absorption pipette. Be sure that the last bubble of gas has been forced into the pipette and that the liquid fills the entire capillary tube; then close the stopcock.

Set the apparatus in motion and allow it to shake for exactly three minutes. Stop the apparatus and immediately turn the stopcock to connect the burette and pipette; draw the remaining gas back into the burette by lowering the aspirator bottle. Be sure that no bubbles of gas remain in the pipette or connecting tube; also be careful to pass the least possible amount of pipette solution into the burette. Then close the stopcock. Allow fifteen seconds for drainage of liquid down the walls of the burette. Remove the aspirator bottle from its stand and hold it so that the liquid in it and in the burette is at exactly the same level and take the burette reading at the lower edge of the meniscus. This reading gives directly the volume of oxygen in ml. that was contained in the sample, and as the total sample taken was 100 ml. the reading indicates the percentage of oxygen in the gas.

A fresh solution should be good for from 60 to 70 tests on commercial oxygen before it becomes spent.

The solution need not be changed until brown solid matter is deposited on the glass of the absorption bottle.

The precipitate deposited in the pipette serves as a warning, but the solution will still give correct results for a few additional tests. Change the burette water at the same time as the pipette solution.

Precautions.—1. Be sure that the glass bottle used for storage of the pipette solution is tightly stoppered to prevent loss of ammonia. A rubber or ground-glass stopper should be used. Corks should never be used with ammonia.

2. Be sure that the water used in the preparation of the solution is distilled water.

3. Do not allow the solutions to come near the mouth, nose or eyes, as painful injury may result.

4. Be sure to keep the stopcock greased. Only a small amount of grease is necessary for this purpose, and care must be taken to remove any excess accumulating in the bore of the stopcock. This can be done with a broom straw or a pipe cleaner.

5. Be sure that the copper coils are kept within ¼ inch of the top of the pipette but that enough free space is allowed to eliminate the trapping of bubbles in this zone.

6. The upper part of the burette is graduated in one-tenth milliliters (0.1 ml.), so that the reading may be made directly to this amount and it should always be estimated to one-half division, or the five one-hundredths of a milliliter (0.05 ml.). Thus if the lower edge of the meniscus is halfway between the 99.50 and the 99.60 marks, the reading is 99.55.

7. Inspect the burette frequently for accumulations of dirt and grease, and, if these are noted, remove and clean the burette. In order to clean a burette the stopcock plug is first removed. The larger particles of grease can then be easily removed by means of a piece of soft copper wire bent at the end. This wire is admitted to the burette through the opening into the stopcock and is moved around until a lump of grease adheres to it. It is then removed, wiped off, and the process repeated. After most of the grease has been removed, a grease film will generally remain on the glass. A small swab of absorbent cotton moistened with carbon tetrachloride and wound tightly around a piece of wire will remove this film. Failure to keep the top of the burette clean may result in errors as great as 0.1%.

AVAILABLE OXYGEN

The determination of the available oxygen in a substance such as manganese dioxide is sometimes demanded on account of the use of an oxidizing agent in various processes, for example in the production of chlorine from hydrochloric acid.

Two procedures are commonly employed: (A) A weighed amount of the dioxide is reduced by a measured amount of standard reducing agent and the excess of the reducing agent determined by titration with standard potassium permanganate, thus establishing the exact amount of reducing agent required by the dioxide.

(B) Indirect method by the liberation of iodine from hydriodic acid by the peroxide (MnO_2, BaO_2, PbO_2 etc.) and titrating the liberated iodine with standard thiosulfate.

Procedure A. Direct Method for Determination of Available Oxygen in Peroxides

Procedure.—The sample is dried to constant weight. If MnO_2 a temperature of 120° C. is permissible.

The theoretical reaction with MnO_2 and reducing agent $FeSO_4$ is as follows:

$$MnO_2+2FeSO_4+2H_2SO_4 \rightarrow MnSO_4+Fe_2(SO_4)_3+2H_2O.$$

Hence 1 ml. of 0.1 N reducing agent is equivalent to 0.00435 g. MnO_2. On the basis of a pure oxide not more than 0.2 gram MnO_2 should be taken. The sample is placed in a 250 ml. Erlenmeyer flask, 50 ml. of water added and 2–5 ml. of concentrated sulfuric acid. The solution is treated with 50 ml. of 0.1 N $FeSO_4$ (or 0.335 g. $Na_2C_2O_4$) standard reagent, the solution heated to near boiling and the excess of $FeSO_4$ titrated immediately with standard 0.1 N $KMnO_4$.

If the normalities of the $FeSO_4$ and $KMnO_4$ are not exactly equivalent, convert to a common basis by titration of say 10 ml. of $FeSO_4$ acidified with H_2SO_4 by $KMnO_4$. From this ascertain the $FeSO_4$ required by the MnO_2.

One gram mole of MnO_2 is equivalent to 32 g. O.

Procedure B. Indirect Method for Determining Available Oxygen in a Peroxide

Procedure.—The reaction with MnO_2 is shown in the following equation:

$$MnO_2+4HCl \rightarrow MnCl_2+2H_2O+Cl_2^{\circ}\uparrow.$$
$$2KI+Cl_2 \rightarrow 2KCl+I_2^{\circ}.$$

In a flask, *B*, Fig. 77, place 15–20 ml. of 20% solution of potassium iodide. Insert in this receiver the side arm a second flask carrying a glass stopper. Place in this second flask about 0.2 gram carefully weighed, of the peroxide (MnO_2). The receiving flask (*B*, see illustration) is cooled by means of ice water. Now add to flask (*A*) about 30 ml. of concentrated hydrochloric acid, quickly replacing the glass stopper. Warm the acid

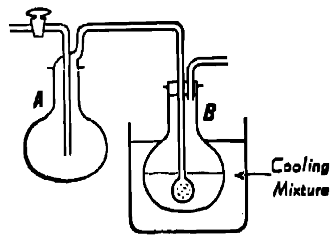


FIG. 77.—Apparatus for Available Oxygen.

gently, distilling the liberated chlorine into the receiving flask containing the KI. Raise the temperature gradually until the acid boils and continue the heating for about five minutes. Without removing the flame lower the flask (*B*). Discontinue heating and titrate the liberated iodine in *B* with standard 0.1 N thiosulfate reagent, using starch indicator.

A blank should be run on the same volume of iodide used in the determination above, diluting to 100 ml., adding 5 ml. HCl and titrating any liberated iodine with standard thiosulfate. This blank should be subtracted from the test above.

Calculate the available oxygen. See Procedure A.

A stream of nitrogen or CO_2 is used to transfer the chlorine to the KI solution.

DETERMINATION OF DISSOLVED OXYGEN IN CYANIDE SOLUTIONS [3]

The method described is a modification of Schutzenberger's whereby the solution in titrations and the standards are protected from the atmosphere by a layer of kerosene. Indigo-disulfonate is the indicator and sodium hydrosulfite the standard. The method is rapid and delicate. It has been tried on a variety of mill solutions and mill men have found the method of value.

The important part that dissolved oxygen plays in the cyanide treatment of gold and silver ores is commonly recognized by most metallurgists and mill men. But heretofore there has been no simple method on which the mill man could rely for determining the amount of oxygen in the various mill solutions.

The method herein described was devised for the use of the mill man, the aim being to develop a simple, practical, accurate method. It is a modification of the Schutzenberger method and depends on the reducing action of a sodium hydrosulfite solution on a solution of indigo blue (indigotin-disulfonate). The method determines oxygen accurately to tenths of a milligram per liter of solution or one part of oxygen in 10,000,000 parts of solution on a 250-ml. solution sample, with a proportionately greater degree of accuracy on larger amounts of solution samples.

Saturation of Oxygen in Solution.—The saturation of oxygen in solution is taken as that maximum quantity of oxygen which dissolves from free air, which is very much less than the quantity of oxygen that dissolves in pure water from an atmosphere of pure oxygen. The amount of oxygen that dissolves in water depends on the atmosphere from which it is derived and, except in the case of hydrogen, this solubility is well explained by Dalton's law of partial pressures of gases. Salts dissolved in the water also affect the oxygen solubility but, under the usual concentrations found in practice, this is relatively unimportant. The oxygen content of air-saturated water is a function of the pressure and temperature; Winkler's results are shown in Fig. 78. From this chart, the saturation point can be quickly determined for all localities and temperatures.

Altitude-pressure and Standard Saturation Curves.—Chart *A*, Fig. 78, is used to determine barometric pressures at various altitudes; chart *B* is used to determine standard saturation values for various temperatures and pressures.

[3] By A. J. Weinig, E.Met., Director of Experimental Plant, Colorado School of Mines, and Max W. Bowen, Golden, Colo.

In chart *A*, altitudes, in feet, are plotted on the horizontal axis and pressures, in millimeters, on the vertical axis. To find the pressure corresponding to a certain altitude, follow the elevation line downward to its intersection with the

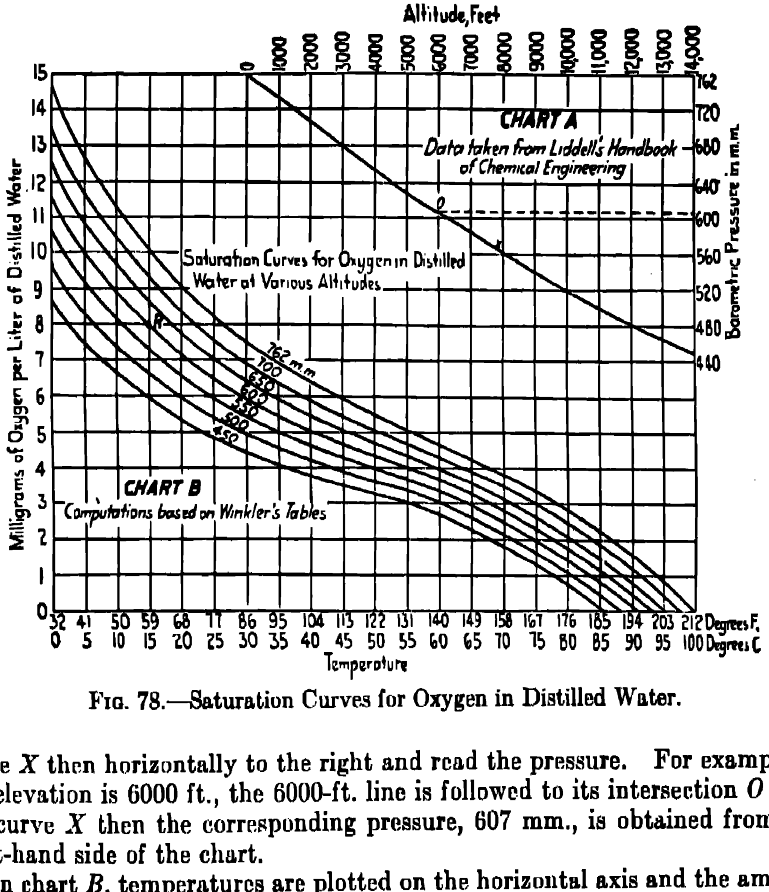


Fig. 78.—Saturation Curves for Oxygen in Distilled Water.

curve *X* then horizontally to the right and read the pressure. For example, if the elevation is 6000 ft., the 6000-ft. line is followed to its intersection *O* with the curve *X* then the corresponding pressure, 607 mm., is obtained from the right-hand side of the chart.

In chart *B*, temperatures are plotted on the horizontal axis and the amount of oxygen, in milligrams per liter of distilled water, is plotted on the vertical axis; various pressure curves also are plotted, as shown. To find the saturation value for a certain temperature and pressure follow the temperature line upwards until the point corresponding to a given pressure is reached, then follow horizontally across to the left-hand side of the chart and read off the amount, in milligrams, of oxygen per liter of solution. For example, to determine the amount of oxygen in a solution having a temperature of 59° F., at an elevation of 6000 ft. It has already been found that at an elevation of 6000 ft. the pressure is 607 mm.; therefore the 607-mm. pressure curve must be used; that is, it is necessary to interpolate between the 600-mm. and the 650-mm. curves. The 59° F. line is followed to its intersection *R* with the 607-mm. curve, then from the left-hand side of the chart is read off 8 mg. of oxygen per liter. The same procedure is used for the various pressures, using the curve corresponding to the particular pressure. For any particular plant, a solubility curve for that elevation should be plotted.

Oxygen-saturated Water or Solution.—The standard for comparison is air-saturated water or solution. This is best made by placing 1 liter of water or solution in a 2-liter Winchester bottle and violently blowing air through it. With distilled water or pure tap water, 20 to 30 minutes' aeration will insure saturation; but with mill solution that contain hydrogen, saturation can only be attained by aerating at least for an hour. Solutions fresh from precipitation saturate with great difficulty; it may take several hours aeration to wash out the dissolved hydrogen before complete oxygen saturation can be attained. After this aeration is completed, the solution should remain for ½ hour or longer at a constant temperature to insure the complete elimination of finely disseminated undissolved air bubbles, which would otherwise interfere. When using water for this standardization, it is well to add a little lime before aeration so as to produce alkalinity similar to the conditions found with cyanide solutions. This alkalinity does not materially affect the solubility of oxygen but is desirable so that the following procedure may be as near like that of cyanide solution as possible. When convenient, it is desirable to use distilled water.

Apparatus.—The apparatus required for this test are: Two Winchester acid bottles *a*, *b*, Fig. 79, 2½ liters capacity; one 250-ml. flask *c*, one 50-ml.

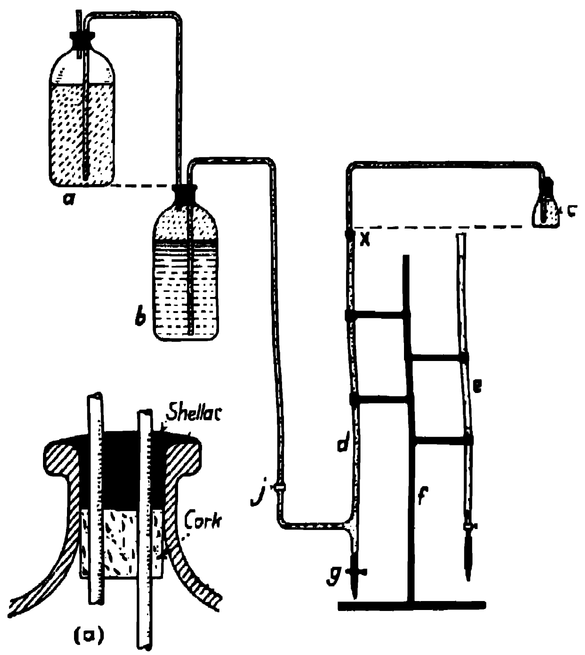


FIG. 79.—Apparatus for Determining Oxygen in Solution.

burette *d* with side connection; one common 50-ml. burette *e*; one clamp stand *f* to hold burettes in position; one 400-ml. beaker with the 250-ml. point marked on it; one special glass stirring rod, shown in Fig. 80; glass or lead tubing (3/16 in.) for connections; rubber tubing for connections; one pinchcock *g* for bottom of rubber connection on burette that contains standard hydrosulfite solution; one container for kerosene to be used in the procedure.

When setting up the apparatus, the relative position of the different parts shown in Fig. 79 must be closely followed. As there is a siphoning action from bottle *a* to bottle *b* and from bottle *b* to the burette *d*, the bottom of bottle *a* must be above the top of bottle *b* and also above the top of the burette *d*; also the bottom of the flask *c* should be above top of the burette *d*, for convenience. Bottle *b* contains the standard solution; as this standard deteriorates very rapidly, if exposed to the air, the bottle must be sealed air tight. This may be done in the following manner: Place a cork—not rubber—with two holes for the tubing in the neck of the bottle so that there is about 1 in. between the top of the cork and the top of the neck of the bottle, as shown in (*a*) Fig. 79. Place the tubing in the cork as shown, then pour melted shellac above the cork so as to fill the space completely. Care must be taken not to break the tubing or the neck of the bottle with the hot shellac; this danger may be avoided by having the glass perfectly dry and heating it before pouring in the hot shellac.

The bottles are filled in the following manner: Remove the connection *x* and place a cork in the top of the burette *d* so that no solution can overflow. Place a bottle containing 2½ liters of kerosene so that its bottom is above the top of bottle *a* and connect this bottle to the bottom of the burette *d* with a siphon. Open the pinchcock *g* and the stopcock *j* and allow kerosene to siphon into bottle *b* until it is filled. Replace the bottle which contained kerosene by a bottle containing the standard solution of hydrosulfite. This solution should always be covered with a layer of kerosene; siphon the standard solution into bottle *b*, the kerosene being forced from bottle *b* over into bottle *a* automatically. As soon as the standard hydrosulfite solution has reached to within 1 or 2 in. of the top of bottle *b*, close both the pinchcock *g* and the stopcock *j*. After the flask *c* has been nearly filled with kerosene, place the connection *x* in top of the burette *d* and seal with dry shellac dissolved in alcohol. Open the stopcock *j*, the pinchcock *g* being kept closed, and allow the standard solution to pass into the burette *d* until it just enters the flask *c*; then close the stopcock *j*, open the pinchcock *g*, and allow the standard solution to drain out completely; its action as a siphon will draw the kerosene over into the burette *d*. The standard solution is now drained off so as to eliminate any possibility of its being exposed to air and to give it a cover of kerosene in the burette *d*. Close the pinchcock *g*, open the stopcock *j*, and allow the burette *d* to fill to the zero mark. The layer of kerosene prevents the admission of air during this procedure. Then the apparatus is ready for use. Fill the burette *e* with the indigo disulfonate solution and place a test tube or glass cover over the top to prevent evaporation.

Standard Solutions.—A very convenient amount of standard sodium hydrosulfite solution is made up as follows. Fill a Winchester acid bottle, 2½ liters capacity, with distilled water. Preferably it should be freshly distilled so as to be as free from oxygen as possible but this is not essential. Dissolve 5 g. of sodium hydroxide in this bottle by gently revolving. When all the sodium hydroxide is dissolved, add 5 g. of sodium hydrosulfite to the solution and immediately place a layer of kerosene over the solution. When all the salts are dissolved, siphon into the bottle *b* for standard solution. The caustic soda preserves the hydrosulfite and enters into the reaction during titration.

The indicator, indigotin disulfonate, is made up as follows: Place in a casserole 7 g. of indigotin and add 30 ml. of concentrated sulfuric acid. Place

over water bath and heat to 90° C. for $1\frac{1}{2}$ hours, or until all lumps disappear. Then dilute to 2 liters with distilled water. Neutralize the acidity by adding powdered limestone, small portions at a time and allowing it to stand for a few minutes between additions, until all action has ceased. Filter without washing, place in a corked bottle, and use as necessary in the procedure. It is convenient to dilute this solution so that 1 ml. of the indicator is equivalent to 0.25 mg. of oxygen per liter of solution. This will indicate 1 g. per liter when a solution sample of 250 ml. is taken for titration.

Standardization of Solutions.—Into the clean, dry, graduated 400-ml. beaker place one drop of phenolphthalein indicator and cover with a $\frac{3}{4}$-in. layer of kerosene. Care should be used to avoid entrapping air bubbles. The oxygen-saturated water is now siphoned into the beaker below the kerosene. The line of demarcation between the kerosene and the solution is very distinct by the red color produced with the indicator in the alkaline water; thereby a close measurement of the water can be attained. When 250 ml. of water have been measured out beneath the kerosene, the alkalinity is neutralized with dilute sulfuric acid from a burette, the tip of which extends below the surface of the solution; 1 ml. of the indigotin disulfonate solution is then run in beneath the kerosene. The solution is now titrated with the hydrosulfite solution. The tip of the burette must dip beneath the kerosene so that, by constant stirring with the special stirring rod (Fig. 80), any entry of air is avoided.

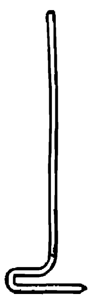


Fig. 80.—Stirrer.

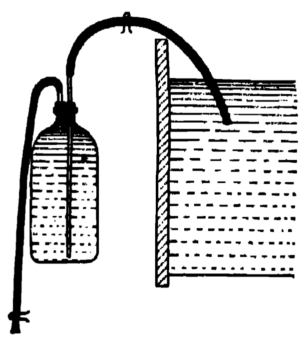


Fig. 81.—Sampling Device for Mill Solutions.

In the titration the hydrosulfite first reacts with the dissolved oxygen; as the end point is reached the hydrosulfite decolorizes the indigo disulfonate and the end point is yellow or yellowish white. When this point is reached, the burette is read and noted and 5 ml. of indigo disulfonate solution is run in, all of the above precautions being taken; this is again followed by titration with the hydrosulfite. This operation gives the required relationships between the various solutions.

Assume that the water showed a saturation of 8 mg. per liter for the particular temperature and pressure, and that the titration gave 9 ml. hydrosulfite standard followed by 5.5 ml. more, after 5 ml. of the indigotin disulfonate standard was added. Then 5 ml. indigotin = 5.5 ml. hydrosulfite; and 1 ml. indigotin = 1.1 ml. hydrosulfite. Also, as 1 ml. of the indigotin was used at the start, we must correct the first hydrosulfite titration for the 1 ml. indigotin used, which is 1.1 ml.

The amount of hydrosulfite then consumed on the dissolved oxygen is, 9.0 ml. – 1.1 ml. = 7.9 ml. Now, 7.9 ml. hydrosulfite = 8 mg. oxygen per liter, or 1 ml. hydrosulfite = $8.0 \div 7.9 = 1.01$ mg. oxygen per liter, when 250 ml. of the saturated water is titrated. Also, 1 ml. indigotin disulfonate standard is equivalent to $\frac{1.1 \times 1.01}{4} = \frac{1.11}{4} = 0.28$ mg. oxygen.

The indigo disulfonate does not deteriorate and may be kept in a well-stoppered bottle. When once standardized, it may be used to check the standard hydrosulfite solution instead of making up aerated water. In this case, sufficient water should be added to the indigo-disulfonate solution until 1 ml. exactly equals 0.25 mg. oxygen.

Titration of Mill Solutions.—When once the hydrosulfite and indigotin-disulfonate solutions are standardized, the procedure with routine solution titrations is simple. The solution is siphoned over beneath the kerosene into the 400-ml. beaker until 250 ml. are obtained, the alkalinity is then neutralized with dilute sulfuric acid, 1 ml. or less of indigotin disulfonate is added as an indicator, and titration is completed with the hydrosulfite. Following this, the necessary correction is made for the indicator and the result is converted to milligrams of oxygen per liter of solution, or per cent saturation as may be desired. The kerosene may be used several times by pouring the contents of the beaker into a large bottle, after titration, then siphoning off the kerosene for reuse after sufficient accumulation.

Precautions.—After the aeration of the solution in the standardization process, sufficient time must be allowed for all entrapped air bubbles to escape before titration or the end-point will " go back " rapidly and erroneous results are obtained.

When stirring the solution during titration, care must be taken not to introduce air into the solution. This stirring is done by revolving the special stirring rod between the thumb and fingers, holding it vertically.

A cover of kerosene should always be kept over the solution.

When mill solutions are used to standardize the hydrosulfite solution, care must be taken that they are thoroughly saturated as they saturate much more slowly than tap or distilled water. It sometimes requires more than an hour to saturate them completely.

The end-point in clear solutions is a slight yellow; but if solutions contain certain salts, or are cloudy, the end-point color may be white or milky, or sometimes gray.

All connections through which the standard solution pass must be sealed air-tight. This is best done with shellac.

When neutralizing the alkalinity of the solution for titration, care must be taken that it is just neutral to phenolphthalein. If it is too acid, the titration will be low; it it is too alkaline, the titration will be too high.

Manipulation in the procedure must be as rapid as possible without sacrificing accuracy, for notwithstanding the cover of kerosene, there will be a slow absorption of oxygen through the kerosene.

If the end-point is over run, back titration can be made with the standard indigo disulfonate; or, if more desirable, an excess of hydrosulfite solution may be run in and the excess titrated with indigo-disulfonate standard.

Sampling of Mill Solutions.—Reasonably clear mill solutions are best sampled by using a bottle, as shown in Fig. 81. This bottle forms part of a siphon, into which a sample may be safely transported to the laboratory. When sampling, the end of the tube that reaches to the bottom of the flask is connected through a pinchcock and tubing to the tank, launder, or other source of solutions to be tested. The tube that just reaches through the cork is also connected to rubber tubing and has a pinchcock. The connections are made as shown and the siphon started by suction. After the bottle is filled with solution, the apparatus is allowed to run for a while to replace any contaminated solutions. The pinchcocks are then closed and the bottle may be transported to the place for titration.

Pulps require settlement before the solutions can be removed for titrations. In this case, it is best to fill a Winchester bottle completely with pulp, close the bottle with its cork, and allow the whole to stand until the solution can be siphoned off.

Examinations made of many operating plant solutions allow the following generalities:

	Per cent of maximum oxygen saturation
General circulating plant solutions	7 to 75
Agitator solutions	0 to 50
Leaching-plant effluent	0 to 50
Crowe vacuum operation removes as a rule, one-half of the oxygen contained in its feed.	
Precipitation plant barrens	0
Concentrate treatment agitator solutions	0

THE DETERMINATION OF OXYGEN IN ORGANIC COMPOUNDS [4, 5]

Many methods for the determination of oxygen in organic compounds have been described.[6] In all these methods it is necessary to perform a *separate* experiment for the determination of oxygen. In the new method proposed the amount of oxygen consumed *during* the combustion of an organic compound *gasometrically* is determined and thus it is possible to analyze for carbon, hydrogen *and* oxygen in *one* operation.

project
assistance for this work has been received from a research fund of the American Petroleum Institute, donated by the Universal Oil Products Co. This fund is being administered by the Institute with the co-operation of the Central Petroleum Committee of the National Research Council.

[5] George Glockler, American Petroleum Institute Research Associate, and L. D. Roberts, Professor of Chemistry, Univ. Southern California, J. Am. Chem. Soc., 50, 828, 1928.

[6] Older work: "Analyse, etc., org. Verbind.," Hans Meyer, 3rd ed., Julius Springer, Berlin, p. 301, 1916; M. C. Boswell, J. Am. Chem. Soc., 35, 284, 1913; 36, 127, 1914; R. Strebinger, Z. anal. Chem., 58, 97, 1919; H. Ter Meulen, Rec. trav. chim., 41, 509, 1922; 43, 899, 1924; Chem. Weekblad, 23, 348, 1926.

The modification of Wise's [7] semi-micro combustion method is used, which has been developed by Dr. W. M. Lauer in the chemical laboratory of the University of Minnesota.

Apparatus and Procedure.—The apparatus used is shown in Fig. 82. Oxygen is made from solid potassium permanganate and measured (N. T. P.) in a Ramsay burette. The combustion tube contains platinized asbestos only. The use of copper oxide is avoided at this time following a suggestion of Professor W. H. Hunter. It is possible that copper oxide wire reduced to copper during the combustion may not be reoxidized to the same extent as it had been originally. The sample is weighed on an ordinary analytical balance, as are the absorption tubes.

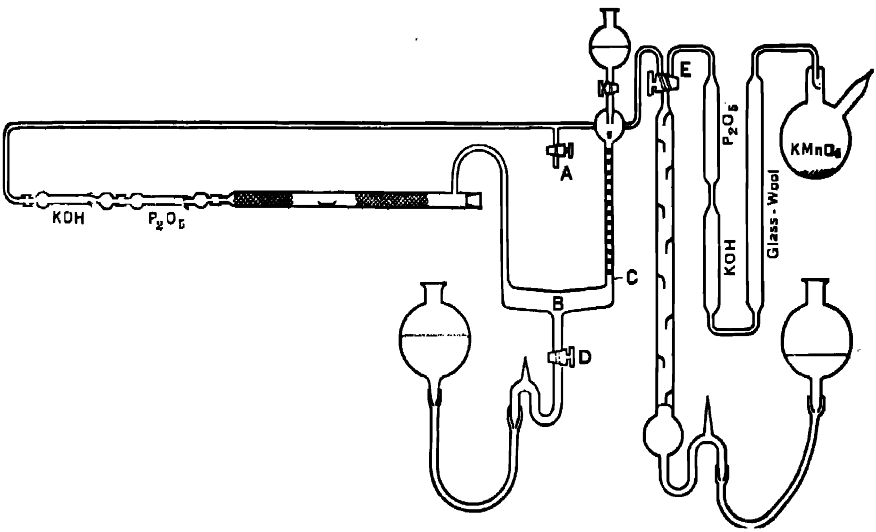


FIG. 82.—Apparatus for Determining Oxygen in Organic Compound.

At the beginning of an analysis the apparatus is brought to atmospheric pressure by opening stopcock *A*. Sample and absorption tubes are, of course, in place. The mercury in vessel *B* is placed on the mark *C* and stopcock *D* is closed. Room temperature and barometer are noted. Oxygen sufficient for the combustion is transferred to the vessel *B* so that all of it would take part in the flow through the combustion tube. The circulation is started by causing the Sprengel pump to operate. By a previous calibration the proper rate of dropping the mercury should be determined so as to produce the usual flow of oxygen through the combustion tube. Forty-five minutes for complete combustion and fifteen minutes for further sweeping is allowed.

At the end of the experiment the apparatus is brought into its initial condition by removing the three pieces of triangular iron which comprised the furnace and all the hot asbestos shields and allowing room temperature to be attained. The remaining oxygen is now removed from vessel *B*, which is again filled with mercury to the mark *C*. Stopcock *D* was closed. The gas is thus transferred to the Ramsay burette, which is set to atmospheric pressure and stopcock *E*

[7] Wise, J. Am. Chem. Soc., 39, 2055, 1917.

is closed. The oxygen remaining in the burette is measured and the absorption tubes are removed and weighed. An analysis can be carried out in two hours.

Blank experiments are run which showed some consumption of oxygen and gain of weight in the potassium hydroxide and pentoxide absorption tubes. However, oxygen thus treated and run through a second blank shows a negligible decrease in volume and the gains in the absorption tubes are also negligible. In further work we expect to pretreat the oxygen as it comes from the generator, thus avoiding the necessity of making blank experiments.

A very important feature of the apparatus is that the system is closed and any gases due to cracking or incomplete combustion (such as methane and carbon monoxide) are carried back through the hot combustion tube several times in the period allowed for the combustion. Thus the method tends to insure complete combustion.

Semi-Micro Determination.—Catalytic hydrogenation may be applied to the direct determination of oxygen in organic substances. Detailed references are given in the chapter on Carbon. The oxygen is weighed in the form of water.

DETERMINATION OF OXYGEN IN STEEL

The properties of steel are affected by the presence of oxygen so that its determination is being recognized as an essential one in the analysis of this product. It occurs in steel as occluded oxygen and as combined oxygen, i.e.

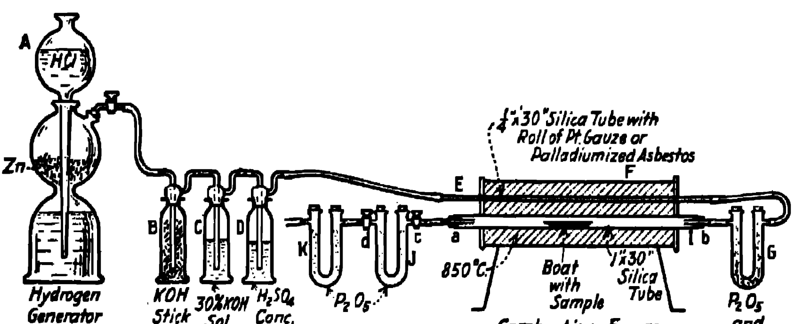


FIG. 83.—Apparatus for Determining Oxygen in Steel.

oxides of iron, aluminum, manganese, silicon, titanium, etc. The following method determines the occluded oxygen and the oxygen combined with iron, but does not determine that combined with manganese, aluminum and silicon, as these oxides are not reduced by hydrogen.

The method depends upon the combination of hydrogen with the oxygen of iron when the latter is heated in a current of hydrogen; the water formed is absorbed and weighed and the oxygen calculated.

The apparatus shown in Fig. 83 gives full details. It is shown that hydrogen generated by the action of HCl on zinc is purified by passing through the wash bottles *B*, *C*, *D*, containing KOH and H_2SO_4, oxygen in the gas is removed by passing through a preheated tube containing platinum gauze or palladiumized asbestos, the water formed being absorbed in the P_2O_5 in *G*. The pure

hydrogen now combines with the oxygen of the sample and the water formed is absorbed in P_2O_5 in the tube *J*.

Procedure. *Preliminary.*—The apparatus is connected up as shown in Fig. 83 and hydrogen gas passed through for 5 to 10 minutes. The P_2O_5 tube is now weighed as in regular test (see notes), the tube being disconnected from *K*, which is used as a guard to prevent moisture being absorbed by an accidental back suction of air.

The sample of 20 to 30 grams of the steel borings are placed in a nickel boat (½″×½″×6″) and this inserted quickly through the opening at "a" into the combustion tube, the current of hydrogen flowing through the tube. The absorption tube *J* and its guard are connected up and the heat turned on. (All connections should be air tight.) The temperature of bright-red heat (850° C.) is desired. The hydrogen is passed at a rate of about 100 ml. per minute, the rate having been previously established by the speed of bubbles in *D*. After 30 minutes the heat is turned off, the top of the hinged furnace lifted, and the tube raised and allowed to cool, hydrogen gas still passing. A blast of air assists the cooling.

The cocks "c" and "d" of *J* are turned off in the order named, the exit end of the guard *K* closed and the two connected placed in the balance for about 10 minutes. The exit end of the guard is now opened, the cock "d" quickly opened and shut, thus obtaining atmospheric pressure in the tube *J* without intake of air. The guard is now disconnected and *J* is weighed. The increase of weight due to absorbed water is multiplied by 0.889 to obtain the weight of occluded oxygen and the oxygen combined with iron.

NOTES.—The tube *J* is weighed before and after the test filled with hydrogen under atmospheric pressure and at the same temperature, so that it is not necessary to aspirate air through the tube as is sometimes recommended. The preliminary run for obtaining the initial weight should be conducted under conditions the same as in the final test, the tubes *J* and *K* being closed, transferred to the balance and *J* finally weighed as stated at the end of the procedure, so that the conditions will be the same in regard to the inclosed hydrogen or the tube.

The P_2O_5 tubes are charged by packing alternate layers of P_2O_5 and glass wool, beginning and ending with the latter, otherwise the powder will pack and prevent the passage of gas.

The drilling of the samples should be done slowly to prevent heating, the drills being free of grease or oil. The samples should be taken from several sections of the ingot, whose surface has been cleaned by a cutting tool or by emery.

The apparatus should be tested for leaks as described in the notes in the chapter on Hydrogen.

DETERMINATION OF FREE OXYGEN IN GAS

1. By Phosphorus.—One hundred ml. of gas are measured out as with the Orsat apparatus, the burette being allowed to drain two minutes. The rubber connectors upon the burette and pipette are filled with water, the capillary tube inserted, as far as it will go, by a twisting motion, into the connector upon the burette, thus filling the capillary with water; the free end of the capillary is inserted into the pipette connector, the latter pinched so as to form a channel for the water contained in it to escape, and the capillary twisted and forced down to the pinchcock. There should be as little free space as possible between the capillaries and the pinchcock. Before using a pipette, its connector (and

rubber bag) should be carefully examined for leaks, especially in the former, and if any found the faulty piece replaced.

The pinchcock on the burette and pipette are now opened, the gas forced over into the phosphorus, and the pinchcock on the pipette closed; action immediately ensues, shown by the white fumes; after allowing it to stand fifteen

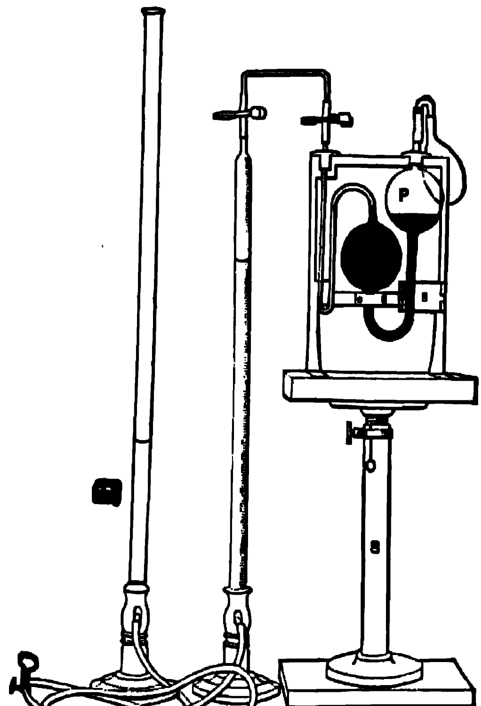


FIG. 84.—Hempel's Apparatus for Determining Oxygen.

minutes the residue is drawn back into the burette, the latter allowed to drain and the reading taken. The absorption goes on best at 20° C., not at all below 15° C.; it is very much retarded by small amounts of ethane and ammonia. It cannot be used to absorb commercial oxygen. No cognizance need be taken of the fog of oxides of phosphorus.

2. **By Pyrogallate of Potassium.**[8]—One hundred ml. of gas [9] are measured out as before, the carbon dioxide absorbed with potassium hydrate and the oxygen with potassium pyrogallate, as with Orsat apparatus; before setting aside the pyrogallate pipette, the number of cubic centimeters of oxygen absorbed should be noted upon the slate *s* on the stand. This must never be omitted with any pipette save possibly that for potassium hydroxide, as failure

[8] See Anderson's work, J. Ind. Eng. Chem., 7, 587, 1915.

[9] A. H. Gill finds after an experience of more than twenty-five years in the laboratory with hundreds of students, that sodium pyrogallate can be used with practically the same results as the potassium compound. The absorption is complete, as shown by subsequent treatment with cuprous chloride.

to do this may result in the ruin of an important analysis. The reason for the omission in this case is found in the large absorption capacity—four to five liters of carbon dioxide—of the reagent.

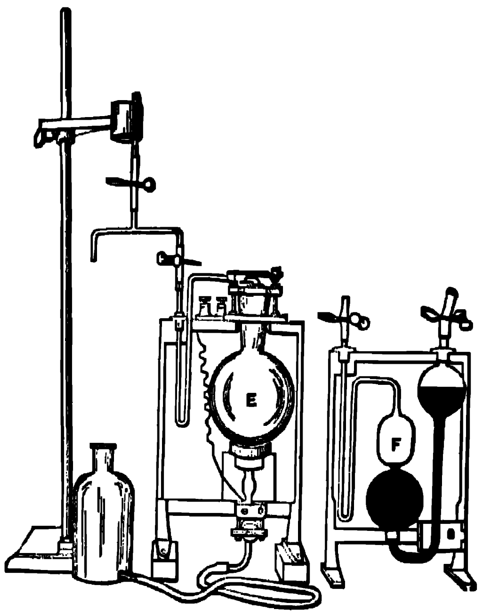


FIG. 85.—Explosion Pipette.

3. **By Explosion with Hydrogen.**—Forty-three ml. of gas and 57 ml. of hydrogen are measured out, passed into the small explosion pipette, the capillary of the pipette filled with water, the pinchcocks and glass stopcock all closed, a heavy glass or fine wire gauze screen placed between the pipette and the operator, the spark passed between the spark wires, and the contraction in volume noted. *The screen should never be omitted, as serious accidents may occur thereby.* The oxygen is represented by one-third of the contraction. For very accurate work the sum of the combustible gases should be but one-sixth that of the non-combustible gases, otherwise some nitrogen will burn and high results will be obtained;[10] that is (H+O) : (N+H) :: 1 : 6.

DETERMINATION OF TRACES OF OXYGEN IN GASES

The apparatus designed by J. G. Dely is shown in the accompanying drawing. The procedure is of special value in the determination of traces of oxygen in the nitrogen-hydrogen gases used in the synthetic catalytic fixation of nitrogen by the Haber or Claud processes or their modifications.

The method depends upon the blue color produced by the action of oxygen on colorless ammoniacal cuprous chloride, and matching with a standard.

Details of the apparatus are shown in Fig. 86. The globe *A* is filled with pure copper drillings. The cylinder *G* contains fine granulated copper. Cupric

[10] This is shown in the work of Gill and Hunt, J. Am. Chem. Soc., 17, 987, 1895.

chloride is reduced in *A* and mixed with the necessary amount of ammonium hydroxide. Complete reduction is effected by slowly flowing the desired portion of the solution through *G* into *H*. Solution in *J* acts as a seal preventing contamination of air.

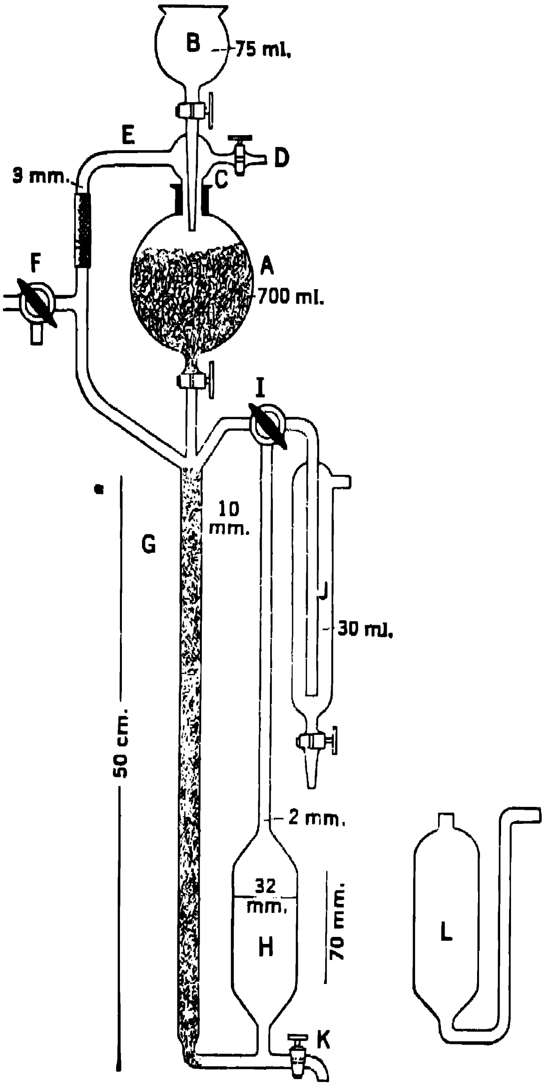


FIG. 86.—Apparatus for Traces of Oxygen in Gases.

Gas in measured quantity is allowed to flow through the solution in *H* until a blue color develops that matches the intensity of color in the standard solution in *L*. The standard has been prepared by passing a known quantity of oxygen through colorless ammoniacal cuprous chloride, under conditions closely matching those of the tested gas.

PHOSPHORUS [1]

P, *at.wt.* 31.02; *sp.gr.* $\begin{cases}\text{yellow } 1.831\\ \text{red } 2.2\end{cases}$; *m.p.* $\begin{cases}44°\text{ C.}\\ 590°\text{ C.}\end{cases}$; *b.p.* $\begin{cases}280°\text{ C.}\\ \ldots\ldots\end{cases}$; *oxides*, P_2O_3, PO_2, P_2O_5; *acids*, H_3PO_2, H_3PO_3, H_3PO_4, HPO_3, $H_4P_2O_7$

Phosphorus occurs combined as phosphate widely distributed in nature in basic igneous rocks and especially rocks high in lime and iron. It occurs in bones, plant and animal tissues and is essential to all living matter. The following minerals are of special interest: apatite (asparagus stone, phosphate rock) $(CaF)Ca_4(PO_4)_3$ or $(CaCl)Ca_4(PO_4)_3$; wavellite, $Al_6(OH)_6(PO_4)\cdot 9H_2O$; vivianite (blue iron earth) $Fe_3(PO_4)_2\cdot 8H_2O$; monazite, essentially (Ce, La, Di)PO_4.

DETECTION

Element.—Phosphorus is recognized by its glowing (phosphorescence) in the air. The element is quickly oxidized to P_2O_5; if the yellow modification is slightly warm (34° C.) the oxidation takes place with such energy that the substance bursts into flame. The red form is more stable. It ignites at 260° C.

Boiled with KOH or NaOH it forms phosphine, PH_3, which in presence of accompanying impurities is inflammable in the air.

Phosphorus oxidized to P_2O_5 may be detected with ammonium molybdate, a yellow compound $(NH_4)_3PO_4\cdot 12MoO_3\cdot 3H_2O$, being formed.

Acids.—***Hypophosphorous Acid, H_3PO_2,*** heated with copper sulfate to 55° C. gives a reddish-black compound, Cu_2H_2, which breaks down at 100° to H and Cu. Permanganates are reduced immediately by hypophosphorous acid. No precipitates are formed with barium, strontium or calcium solutions. Zinc in presence of sulfuric acid reduces hypophosphorous acid to phosphine, PH_3.

Phosphorous Acid, H_3PO_3.—Copper sulfate is reduced to metallic copper and hydrogen is evolved, no Cu_2H_2 being formed as in case of hypophosphorous

[1] The element was first obtained from urine in 1674 by the alchemist Brand in his search for the philosopher's stone. His discovery was confirmed by Boyle in 1680. In 1771 Scheele obtained the element from burnt bones. The element was formerly used in the manufacture of matches, a practice discontinued on account of serious poisoning by the yellow modification. Red phosphorus now forms the coating on the box of the safety match. Combined phosphorus, in form of phosphates of calcium, is valuable as a fertilizer.

acid. Permanganates are reduced slowly. Added to solutions of barium, strontium or calcium white phosphites of these elements are precipitated. Alkali phosphites are soluble in water, while hypophosphites are not readily soluble.

Orthophosphoric Acid, H_3PO_4.—Ammonium phosphomolybdate precipitates yellow ammonium phosphomolybdate from slightly nitric acid solutions. The precipitate is soluble in ammonium hydroxide.

Metaphosphoric Acid, HPO_3.—Converted by nitric acid in hot solutions to the ortho form. Metaphosphoric acid is not precipitated by ammonium molybdate.

Pyrophosphoric Acid, $H_4P_2O_7$.—Converted to orthophosphoric acid in hot solutions by nitric acid. No precipitate is formed with ammonium molybdate.

COMPARISON OF ORTHO, META AND PYROPHOSPHORIC ACIDS

Reagent	Orthophosphoric acid	Metaphosphoric acid	Pyrophosphoric acid
Ammonium molybdate	Yellow ppt.	No ppt.	No ppt.
Albumin	——	Coagulated	Not coagulated
Zinc sulfate, cold, in excess	——	No ppt.	White ppt.
Silver nitrate in neutral solution	Yellow ppt., Ag_3PO_4	White ppt., $AgPO_3$	White ppt., $Ag_4P_2O_7$
Magnesium salts	White ppt.	No ppt.	No ppt.

Phosphorous acids are distinguished from phosphoric acids by the phosphine formed with the former when acted upon with zinc.

Acid phosphates are distinguished from normal phosphates as follows: Neutral silver nitrate added to an acid phosphate liberates free nitric acid (Litmus test), the following reaction taking place:

$$3AgNO_3+Na_2HPO_4=Ag_3PO_4+2NaNO_3+HNO_3.$$

The solution resulting when silver nitrate is added to normal phosphate solution is neutral.

$$3AgNO_3+Na_3PO_4=Ag_3PO_4+3NaNO_3.$$

ESTIMATION

The determination of the pentoxide of phosphorus is required in a large number of substances, since it is widely distributed in the form of phosphates.

The chemist is especially concerned in the determination of phosphoric acid (P_2O_5), in the evaluation of materials used for the manufacture of the

acid: bone ash and phosphate rock (see table below). Generally, determinations of lime, iron and alumina are also desired and frequently a more complete analysis. In the analysis of phosphoric acid certain impurities occurring in the crude material used are determined, e.g., iron, lime, magnesia, sulfuric, hydrochloric and hydrofluoric acids, etc. Phosphoric acid is determined in the evaluation of phosphate fertilizers, phosphates used in medicine, phosphate baking powders, etc.

The element is determined in iron, steel, phosphor bronzes, and other alloys.

TYPICAL ANALYSES [2]

Substance	Bone ash	Charlestown phosphate	Spanish phosphorite	Sombrero phosphate	Redonda phosphates	Canadian phosphate
Phosphoric oxide..	39.55	27.17	33.38	35.12	35.47	37.68
Sulfur trioxide....	——	3.30	0.57			
Carbon dioxide....	4.43–	4.96	4.10	7.40		
Lime............	52.46	44.03	47.16	51.33	——	51.04
Magnesia.........	1.02	0.37	trace			
Alumina.........	——	1.44	0.89	+Fe	20.17	Fe_2O_3,
Ferric oxide......	0.17	0.43	2.59	1.02	8.85	Al_2O_3
Fluorine, etc......	——	2.38	4.01	——	——	F. etc.
Alkaline salts.....	——	0.87	——	0.42		=6.88
Silica—sand, etc...	0.51	5.60	3.71	2.02	9.70	4.29

A portion of the phosphate during the analysis may be carried down with the insoluble silica residue, especially in presence of tin, titanium, thorium and zirconium, some of which will volatilize with the SiF_4 during the heating with $HF \cdot H_2SO_4$. It is advisable to provide for the determination of phosphorus in the initial material. The phosphate remaining in solution will precipitate with the aluminum precipitate when the solution is made alkaline with NH_4OH, phosphates of iron, aluminum, titanium, calcium, etc., being insoluble in NH_4OH.

Decomposition of the material is generally effected by action of nitric acid. In metallurgical products in which phosphides are present the same precautions of oxidation are necessary as in case of sulfur determinations where a loss of H_2S is avoided, since with a phosphide a loss would result by volatilization of phosphine. Fusions with $KHSO_4$ at high temperature should be avoided. Transposition of phosphates to the water soluble sodium salt takes place by fusing the material with Na_2CO_3.

Preliminary Remarks.—Practically all procedures for the determination of phosphorus depend upon its oxidation to orthophosphoric acid and its precipitation by ammonium molybdate from a nitric acid solution as ammonium phosphomolybdate. It may now be determined either gravimetrically or volumetrically. Two procedures are of importance in the gravimetric determination of phosphorus; the first depends upon the direct weighing of the yellow phosphomolybdate, dried at 110° C.; the second, on the conversion of the yellow precipitate to the magnesium salt and its ignition to pyrophosphate. Two volumetric procedures, which are of special value in the determination of small amounts of phosphorus as in case of phosphorus in iron and steel, are

[2] Thorpe, "Dictionary of Applied Chemistry," Longmans, Green & Co.

to be recommended for their rapidity and accuracy. One of these is to dissolve the ammonium phosphomolybdate in a known amount of standard caustic, titrate the excess of alkali with standard acid, which indicates the alkali required to neutralize the molybdic acid in the yellow precipitate. From this the amount of phosphorus present may be calculated. A second procedure of equal accuracy and rapidity is to dissolve the molybdate in ammonia, add an excess of sulfuric acid, pass the warm solution through a column of zinc and titrate the reduced molybdic acid with standard potassium permanganate, the amount of permanganate required being a measure of the phosphorus present.

The impurities interfering in the procedures are silica and arsenic acid. The first may be eliminated by dehydration of the silicic acid in the solution and its removal as insoluble SiO_2 by filtration. Arsenic in small quantities does not interfere under certain conditions; in large quantities its removal is imperative.

PREPARATION AND SOLUTION OF THE SAMPLE

Amount of the Sample Required.—For accurate results it is advisable to take a fairly large sample, 5 to 10 grams, and when it has been dissolved, to dilute to a definite volume, 500 or 1000 ml. Aliquots of this solution are taken for analysis.

Iron Ores, Phosphate Rock and Minerals.—Five to 10 grams of the pulverized material placed in a 3-in. porcelain dish are digested for an hour with nitric acid, the dish being covered by a clock-glass and placed on a steam bath. The acid is now diluted with half its volume of water and the solution filtered into a porcelain dish of sufficient capacity to hold the filtrate and washings. The residue is washed with dilute nitric acid (1 : 1) until free of visible iron discoloration. The filtrate and washings are evaporated rapidly on a hot plate to small volume and then to dryness over the steam bath. Meanwhile the *insoluble residue* and filter are ignited in a 20-ml. platinum crucible over a Méker burner or in a muffle furnace and the residue fused with ten times its weight of sodium carbonate. The fusion is removed by inserting a platinum wire into the molten mass, allowing to cool and then gently heating until the mass loosens from the crucible, when it may be removed on the wire. The cooled mass on the wire and that remaining in the crucible are dissolved in dilute nitric acid, and the filtered solution added to the main solution. The combined solutions are evaporated to dryness, and heated gently to dehydrate the silica. The residue is taken up with a few ml. of nitric acid, the solution diluted, filtered and the SiO_2 washed with dilute nitric acid solution. The combined filtrates are made up to 500 or 1000 ml. Aliquots of this solution are taken for analysis.

Iron and Steel.—Five to 10 grams of the drillings or filings are dissolved in an Erlenmeyer flask with 50 to 100 ml. of dilute nitric acid (1 : 1), more acid being added if necessary. When dissolved, a strong solution of $KMnO_4$ is added until a pink color appears; on boiling brown manganese dioxide forms in the solution if a sufficient amount of permanganate has been added. This is dissolved by adding 2% sodium sulfite solution in just sufficient quantity to dissolve the precipitate. The solution is diluted to a convenient volume for

analysis. Where a number of determinations are to be made, it is advisable to weigh the amount of sample desired for the determination and to precipitate the ammonium phosphomolybdate in the flask in which the drillings have been dissolved.

Ferro-Silicon, Iron Phosphide and Acid Insoluble Alloy Steels.—Decomposition is best accomplished by fusing 1–2 grams with 10–15 grams of a mixture of sodium carbonate and magnesium oxide (2 : 1). (A blank should be run on the reagents and allowance made for any phosphorus present.) The fusion is dissolved in HCl, HNO_3 added and then the solution evaporated to dryness and the SiO_2 filtered off. The SiO_2 is treated with HF and a few drops of H_2SO_4 in a platinum dish and taken to fumes. The residue is fused with Na_2CO_2, and the fusion dissolved in HNO_3 and the solution added to the main filtrate containing the iron and phosphate, etc. This filtrate is concentrated to near dryness, 10 ml. nitric acid added and the evaporation repeated. This concentrate is diluted to about 25 ml. and phosphorus precipitated with ammonium molybdate solution as usual.

Ferro-Titanium, Metallic Titanium.—The fusion, obtained as directed for ferro-silicon, is extracted with water to dissolve out the sodium phosphate. The residue is fused with sodium carbonate and again extracted with water. The water extracts of the two fusions is examined for phosphorus. The extracts are made acid with nitric acid, the solution evaporated to near dryness, nitric acid added and the concentrated solution treated as directed for steel. Iron, in this case, has been removed with titanium.

Materials Containing Tungsten.—The alloy is dissolved in dilute HNO_3 and evaporated to dryness, HNO_3 is now added and the solution again evaporated to dryness, the residue is taken up with HNO_3 and again evaporated. This residue is extracted with dilute HNO_3 and washed with acid ammonium nitrate. Iron and phosphorus are in solution, Si and W remain insoluble.

Ores Containing Titanium.—Titanium may be recognized by the red color produced by hydrogen peroxide, H_2O_2, added to the sulfuric acid extract; also by the reduction test with zinc, which causes a play of colors, the solution becoming colorless by the reduction of iron, then, in presence of titanium, pink, purple and finally blue. (Vanadium gives similar tests.) Solutions containing titanium frequently appear milky when the solution is diluted before filtering off the insoluble residue. Since titanium forms an insoluble compound with phosphoric acid and iron oxide the final residue, obtained by the method of solution for ores, phosphate rock and minerals, should be moistened with sulfuric acid and the silica expelled with hydrofluoric acid. The solution is evaporated to dryness and to SO_3 fumes, the residue fused with sodium carbonate and taken up with boiling water. TiO_2 remains insoluble, while P_2O_5 passes into the filtrate.

Determination of Phosphorus in Organic Matter.—Decompose the organic matter with nitric acid in a sealed tube according to the method of Carius, chapter on Chlorine, and determine the phosphoric acid formed. The Kjehldahl digestion may also be used to decompose organic matter. (Selenium is used as catalyst.)

Soluble Phosphates, Phosphate Baking Powder, etc.—A water extract is generally sufficient to get the material in solution. In case iron, alumina, lime and magnesia salts are present, as may occur in baking powders, an ex-

traction with dilute 3% nitric acid is necessary. It is advisable to dissolve a 5- to 10-gram sample and take an aliquot part of the solution made up to a definite volume. Before precipitating with ammonium phosphomolybdate, 5 grams of ammonium nitrate should be added for each gram of the sample taken for analysis.

GRAVIMETRIC METHODS FOR DETERMINATION OF PHOSPHORUS

A. DIRECT WEIGHING OF THE AMMONIUM PHOSPHOMOLYBDATE

Precipitation of ammonium phosphomolybdate is common to all subsequent methods for determination of phosphorus.

Reaction.—

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 = (NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 12H_2O.$$

Amount of Sample Required for Analysis.—In volumetric procedures the amount of sample should be such that the phosphorus content will be between 0.005 and 0.0005 gram phosphorus. In gravimetric procedure twice this amount is desirable.

Ammonium Molybdate Reagent.—See page 697, and the chapter on Reagents.

Precipitation.—The free acid of the solution is nearly *neutralized* by *addition of ammonium hydroxide.* In analysis of phosphate rock or materials comparatively low in iron, it is advisable to add ammonium hydroxide in quantity sufficient to cause a slight permanent precipitate followed by just sufficient HNO_3 to dissolve the precipitate. In *iron and steel* analysis ammonium hydroxide is added until the precipitated iron hydroxide dissolves with difficulty and the solution becomes a deep amber color or cherry red. In analysis of *soluble phosphates,* litmus paper dropped into the solution indicates the neutral point. *Nitric acid* is added to the neutral or slightly acid solution, 5 ml. of acid for every 100 ml. of solution. A volume of 150 to 200 ml. of solution is the proper dilution for samples taken in amounts above recommended. To the warm solution (not over 45° C.) *ammonium molybdate is added,* 60 ml. of the reagent being required for every 0.1 gram of P_2O_5 present.[3] The solution is stirred, or shaken, if in a flask, until a cloudy precipitate of ammonium phosphomolybdate appears. It is then allowed to settle without further heat-

[3] Ten–twenty-five fold excess is generally necessary. One hundred fold may be necessary. HCl, HF, H_2SO_4 retard precipitation. Organic matter, V, Ti and Zr should not be present.

ing for an hour. The filtrate should be tested with additional ammonium molybdate for phosphorus. The yellow precipitate is filtered and washed with 1% HNO_3 solution followed by a 1% solution of KNO_3, or NH_4NO_3 or $(NH_4)_2SO_4$ as the special case requires. Filtration through asbestos in a Gooch crucible is to be recommended. When a large number of determinations are to be made, as in case of iron and steel, filter paper is more convenient.

A. Direct Weighing of the Ammonium Phosphomolybdate

The sample being dissolved and the ammonium phosphomolybdate precipitated according to directions already given above, the supernatant solution is filtered through a weighed Gooch crucible and washed twice by decantation with dilute nitric acid (1%), the precipitate washed into the Gooch, followed by two washings with 1% KNO_3 or NH_4NO_3 (neutral solutions) and finally with water. The precipitate, free from contaminating impurities, is dried for two hours in an oven at 110° C., then cooled in a desiccator and weighed. Weight of precipitate $\times 0.0165 = P$, or $\times 0.03783 = P_2O_5$.

B. DETERMINATION OF PHOSPHORUS AS MAGNESIUM PYROPHOSPHATE

Magnesia Mixture.—For precipitation of ammonium magnesium phosphate, 110 grams of magnesium chloride ($MgCl_2 \cdot 6H_2O$) are dissolved in a small amount of water. To this are added 280 grams of ammonium chloride and 700 ml. of ammonia (sp.gr. 0.90); the solution is now diluted to 2000 ml. with distilled water. The solution is allowed to stand several hours and then filtered into a large bottle with glass stopper. Ten ml. of the solution should be used for every 0.1 gram P_2O_5 present in the sample analyzed. As the reagent becomes old it will be necessary to filter off the silica that it gradually accumulates from the reagent bottle. See method for reagent as prepared by McCandless and Burton under *Notes.*

Procedure.—The ammonium phosphomolybdate, obtained as previously directed, is filtered onto a filter paper and washed four or five times with dilute 1% HNO_3. The precipitate is now dissolved from the filter by a fine stream of hot ammonium hydroxide (1 : 1), catching the solution in the beaker in which the precipitation was made. The solution and washings should be not over 100 to 150 ml. Hydrochloric acid is added to the cooled solution to neutralize the excess of ammonia, the yellow precipitate, that forms during the neutralization, dissolving with difficulty, when sufficient acid has been added. To the cooled solution *cold magnesia mixture is added* drop by drop (2 drops per second) with constant stirring. Ten ml. of the reagent will precipitate 0.1 gram P_2O_5. When the solution becomes cloudy the stirring is discontinued and the precipitate allowed to settle ten minutes. *Ammonium hydroxide is added* until the solution contains about one-fourth its original volume of conc. ammonia (e.g. 25 ml. NH_4OH, 90 to 100 ml. of solution). The solution is stirred during the addition and then allowed to settle for at least two hours. It is filtered through filter paper and the precipitate washed with dilute ammonium hydroxide (1 : 4). It is generally advisable to redissolve the compound and again precipitate the magnesium ammonium phosphate. The precipitate is then placed in a porcelain crucible, a few drops of saturated solution of ammonium nitrate added and the precipitate heated

over a low flame till decomposed (or until the paper chars). The lumps of residue are broken up with a platinum rod and again ignited over a Scimatico or Méker burner, the heat being gradually increased to 1100° C. If the heating is properly conducted, the resultant ash will be white or light gray, otherwise it will be dark. The addition of solid ammonium nitrate aids the oxidation in obstinate cases, but there is danger of slight mechanical loss.[4] The crucible is cooled in a desiccator and the residue weighed as magnesium pyrophosphate

$$Mg_2P_2O_7 \times 0.2786 = P \quad \text{and} \quad Mg_2P_2O_7 \times 0.6379 = P_2O_5.$$

DIRECT PRECIPITATION OF MAGNESIUM AMMONIUM PHOSPHATE

In the absence of heavy metals whose phosphates are insoluble in an ammoniacal solution, the magnesia mixture may be added directly to the slightly acid solution containing the phosphate, and then make ammoniacal by adding NH_4OH without previous precipitation of ammonium phosphomolybdate. The magnesium ammonium phosphate is washed and ignited according to directions given above, and weighed as magnesium pyrophosphate. Consult the chapter on Magnesium.

NOTES.—J. M. McCandless and J. I. Burton, J. Ind. Eng. Chem., 19, 406, 1927, recommend the following method of preparing the magnesia mixture:

Dissolve 22 grams of recently ignited calcined magnesia in dilute hydrochloric acid, avoiding an excess of the acid. Add a little calcined magnesia in excess and boil a few minutes to precipitate iron, alumina, and phosphoric acid. Filter into a 2-liter flask. Add hydrochloric acid dropwise, using methyl orange as indicator, until the solution just reacts acid, then add 1 ml. of 1 : 1 hydrochloric acid. Add 280 grams of ammonium chloride, make to mark, and filter into the stock bottle. From this solution any small quantity of magnesia mixture may be quickly and easily made. If 100 ml. are desired, take 50 ml. of the stock solution, add to it 13 ml. of ammonia (sp.gr. 0.90) and make up to 100 ml. Filter just before using. Fifteen ml. of this solution are ample for each decigram of P_2O_5.

Other Methods.—The precipitation of phosphomolybdic acid from approximately 2N H_2SO_4 solution by a saturated solution of nitratopentammine cobaltic nitrate gives a compound of high molecular weight, $[Co(NH_3)_5NO_3]H_3PMo_{12}O_{41}$, suitable for the estimation of amounts of phosphorus ranging from 0.6–16 mg. in the presence of 50–100 mg. of ferric ion or calcium ion. *Procedure.* Add 6 ml. of 6N H_2SO_4 to the phosphate solution, and evaporate to 6–8 ml. (or to fumes of SO_3 if HCl, HNO_3 or H_2F_2 are present), add 1 ml. of sodium molybdate (0.2 g. MoO_3 per ml.) per each mg. of P expected to be present, and enough saturated cobalt reagent (8.5 g. per liter) to color the liquid pink, then 3–5 ml. in excess. Stir and heat at 90° for 5 minutes. If necessary evaporate to 18–20 ml. Cool to room temperature, filter through a weighed filter crucible, wash free of H_2SO_4 with 0.3 N HNO_3, wash once with a little water, then with 3 five ml. portions of alcohol and finally

[4] W. M. McNabb (J. Am. Chem. Soc., 49, 891, 1927, has shown that loss of P_2O_5 occurs if ignition of $MgNH_4PO_4$ is carried on with free HNO_3, but no loss in presence of free NH_4OH. Therefore moistening the residue with HNO_3 should not be done, as is sometimes recommended.

with two 5 ml. portions of ether. Let stand 30 min. in a vacuum desiccator, and weigh. Wt. ppt. $\times$0.01515 = wt. P or $\times$0.03468 = wt. P_2O_5 found.[5]

VOLUMETRIC METHODS FOR THE DETERMINATION OF PHOSPHORUS

These volumetric procedures are especially applicable for determining small amounts of phosphorus such as are present in steel and in alloys.

C. ALKALIMETRIC METHOD

The method is based on the acid character of ammonium phosphomolybdate, the following reaction taking place with an alkali hydroxide:

$$(NH_4)_3PO_4 \cdot 12MoO_3 + 23NaOH = NaNH_4HPO_4 + (NH_4)_2MoO_4 + 11Na_2MoO_4 + 11H_2O.$$

From the reaction 46 molecules of sodium hydroxide are equivalent to one molecule of P_2O_5, hence 1 ml. of N/10 solution of sodium hydroxide neutralizes the yellow precipitate containing an equivalent of .000309 gram of P_2O_5. (N equivalent of P = 31.02 ÷ 23 = 1.35.)

Solutions Required. ***Nitric Acid for Dissolving.***—Mix 1000 ml. of HNO_3, sp.gr. 1.42, and 1200 ml. of distilled water.

Nitric Acid for Washing.—Mix 20 ml. of HNO_3, sp.gr. 1.42, and 1000 ml. of distilled water.

Ammonium Molybdate.—Solution No. 1. Place in a beaker 100 g. of 85% molybdic acid, mix it thoroughly with 240 ml. of distilled water, add 140 ml. of NH_4OH, sp.gr. 0.90, filter and add 60 ml. of HNO_3, sp.gr. 1.42.

Solution No. 2. Mix 400 ml. of HNO_3, sp.gr. 1.42, and 960 ml. of distilled water.

When the solutions are cold, add solution No. 1 to solution No. 2, stirring constantly; then add 0.01 gram of ammonium phosphate dissolved in 10 ml. of distilled water and let stand at least 24 hours before using.

Potassium Nitrate, 1%.—Dissolve 10 g. of KNO_3 in 1000 ml. of distilled water.

Phenolphthalein Indicator.—Dissolve 0.2 g. of phenolphthalein in 50 ml. of 95% ethyl alcohol and 50 ml. of distilled water.

Standard Sodium Hydroxide.—Dissolve 6.5 g. of purified NaOH in 1000 ml. of distilled water, add a slight excess of 1% solution of barium hydroxide, let stand for 24 hours, decant the liquid, and standardize it against a steel of

[5] Furman and State, Ind. Eng. Chem., Anal. Ed., 8, 420 (1936).

known phosphorus content as determined by the molybdate-magnesia method, so that 1 ml. will be equivalent to 0.01% of phosphorus on the basis of a 2-g. sample (see notes). A 0.1 N or N/10 solution contains 4 g. NaOH (100%) per 1000 ml.

Protect the solution from carbon dioxide with a soda-lime tube.

Ferric Chloride.—Dissolve 100 g. of ferric chloride (phosphorus free) in 100 ml. of distilled water.

Standard Nitric Acid.—Mix 10 ml. of HNO_3, sp.gr. 1.42, and 1000 ml. of distilled water. Titrate the solution against standardized NaOH, using phenolphthalein as indicator, and make it equivalent to the NaOH by adding distilled water. 0.1 N or N/10 solution contains 6.3 g. HNO_3 per 1000 ml.

Determination of Phosphorus in Ores and Minerals.—See page 692.

Determination of Phosphorus in Iron and Steel.—See Vol. II.

DETERMINATION OF PHOSPHORUS IN COPPER ALLOYS

In a 400-ml. casserole dissolve 1 g. of copper alloy metal in 10 ml. of HNO_3, sp.gr. 1.42. Add 20 ml. of HCl, sp.gr. 1.20, and evaporate to dryness. Moisten with HCl, evaporate to dryness again, and bake to dull redness. Moisten with HCl again (add 3 ml. of ferric chloride solution unless iron is already present) and dilute to about 200 ml. with distilled water. Add NH_4OH, sp.gr. 0.90, until the basic salts of copper have dissolved and the solution has become a deep blue. Boil, allow to settle, and filter on a loosely woven filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitate on the filter with hot dilute HCl, dilute the solution to about 200 ml., add NH_4OH, sp.gr. 0.90, until the precipitate which forms at first dissolves rather slowly, and saturate with H_2S gas. Filter off and reject the precipitate. Boil the filtrate to expel H_2S, and add HNO_3, sp.gr. 1.42, until the iron is oxidized. Add NH_4OH, sp.gr. 0.90, until the solution is alkaline. Boil and filter on a loosely woven filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitate on the filter with HNO_3 (sp.gr. 1.42), receiving the solution in a 350-ml. Erlenmeyer flask. Add NH_4OH, sp.gr. 0.90, until the iron is entirely precipitated, and then add HNO_3, sp.gr. 1.42, cautiously until the solution just becomes clear. Bring the solution to a temperature of about 60° C., and add 40 ml. of ammonium molybdate at room temperature. Allow to stand for one minute, shake or agitate for 3 minutes, and filter on a 9-cm. paper. Wash the precipitate three times with the 2% HNO_3 solution to free it from iron, and continue the washing with the 1% KNO_3 solution until the precipitate and flask are free from acid.

Transfer the paper and precipitate to a solution flask, add 20 ml. of distilled water, 5 drops of phenolphthalein solution as indicator, and an excess of standard NaOH solution. Insert a rubber stopper and shake vigorously until solution of the precipitate is complete. Wash off the stopper with distilled water and determine the excess of NaOH solution by titrating with standard HNO_3 solution. Each milliliter of standard NaOH solution represents 0.01% of phosphorus.

Accuracy.—Duplicate determinations should check within 0.01% of phosphorus.

NOTES.—The ammonium molybdate solution should be kept in a cool place and should always be filtered before using.

All distilled water used in titrations should be freed from carbon dioxide by boiling or otherwise.

METHOD FOR STEEL

Procedure. Preparation of the Sample.—Consult pages 692 and 693. After oxidation of the sample by adding a strong solution of $KMnO_4$ and boiling, and dissolving the precipitated MnO_2 by reduction with sodium sulfite, the greater part of the free acid is neutralized by addition of ammonia. The solution will appear a deep cherry red color. No iron precipitate should be present. Ammonium phosphomolybdate is now precipitated by addition of ammonium molybdate according to the procedure outlined on page 694. This is filtered into a Gooch crucible containing asbestos, and washed once or twice with water containing 1% nitric acid, and then several times with a 1% neutral solution of potassium nitrate until the washings are free of acid, as indicated by testing with litmus paper. The asbestos mat containing the precipitate is transferred to a No. 4 beaker, 100 ml. of CO_2 free water added, followed by about 20 ml. of N/10 NaOH measured from a burette. The crucible is rinsed out with 5 to 10 ml. of N/10 NaOH, the exact amount being noted and then with water, adding the rinsings to the main solution. Phenolphthalein indicator is added, and the excess of caustic titrated with N/10 HNO_3.[6] The total NaOH added minus the acid titration equals the ml. of the caustic required to react with the yellow precipitate.

One ml. of 0.1 N or N/10 NaOH = 0.000135 gram of P.

The exact factor should be determined as directed under Reagents.

(*b*) **Method for Ores.**—See page 692.

D. ZINC REDUCTION AND TITRATION WITH POTASSIUM PERMANGANATE

Permanganate. Ferric-Alum Method.—This method is based on the assumption that ammonium phosphomolybdate $(NH_4)_3 \cdot 12MoO_3 \cdot PO_4$, is reduced, in acid solution, by zinc, the molybdic acid, MoO_3, forming the lower oxide Mo_2O_3, in which form it reacts with ferric iron in the receiving flask, reducing a corresponding equivalent of ferric salt to ferrous condition, being itself oxidized to MoO_3. When the ferric solution is not placed in the receiving flask, a slight oxidation takes place, the oxide $Mo_{24}O_{37}$ apparently being formed.

Special Apparatus Required. ***Jones' Reductor.***—Details of the reductor are given under the determination of iron by the permanganate method, also under the Volumetric Determination of Molybdenum.

Solutions Required. ***Dilute Ammonia.***—Mix 100 ml. of NH_4OH, sp.gr. 0.90, and 900 ml. of distilled water.

Dilute Hydrochloric Acid.—Mix 500 ml. of HCl, sp.gr. 1.20, and 500 ml. of distilled water.

Dilute Sulfuric Acid for Dissolving.—Mix 200 ml. of H_2SO_4, sp.gr. 1.84, and 800 ml. of distilled water.

[6] If a large quantity of yellow precipitate is present, five minutes should be allowed for the alkali to react before titrating the excess with standard acid.

Dilute Sulfuric Acid for Reductor.—Mix 500 ml. of H_2SO_4, sp.gr. 1.84, and 500 ml. of distilled water.

Ammonium Molybdate.—Solution No. 1. Place in a beaker 100 g. of 85% molybdic acid, mix it thoroughly with 240 ml. of distilled water, add 140 ml. of NH_4OH, sp.gr. 0.90, filter and add to 60 ml. of HNO_3, sp.gr. 1.42.

Solution No. 2. Mix 400 ml. of HNO_3, sp.gr. 1.42, and 960 ml. of distilled water.

When the solutions are cold, add solution No. 1 to solution No. 2, stirring constantly, then add 0.1 g. of ammonium phosphate dissolved in 10 ml. of distilled water, and let stand at least 24 hours before using.

Acid Ammonium Sulfate.—Mix 25 ml. of H_2SO_4, sp.gr. 1.84, and 1000 ml. of distilled water, and then add 15 ml. of NH_4OH, sp.gr. 0.90.

Ferric Alum.—Dissolve 200 g. of ferric ammonium sulfate crystals in 1950 ml. of distilled water. Add 50 ml. of H_2SO_4, sp.gr. 1.84, and 80 ml. of phosphoric acid, 85%.

Potassium Permanganate.—Dissolve from 3.0 to 3.2 g. of $KMnO_4$ in 1000 ml. of distilled water. Allow the solution to stand for about one week, and then filter it through an asbestos filter. Standardize by using about 0.200 g. portions of pure sodium oxalate—29.85 ml. of 0.1 N solution. See Chapter on Reagents.

Standard for Phosphorus in Steel.—The exact value of the permanganate solution may be accurately and rapidly determined in terms of phosphorus by standardizing against a sample of standard steel containing a known amount of phosphorus, the ultimate standard being steel drillings furnished by the Bureau of Standards. The drillings are dissolved in nitric acid, oxidized with $KMnO_4$, the excess of the reagent being destroyed by sulfite solution. Ammonia is added until the solution becomes a deep amber color. The phosphorus is precipitated as ammonium phosphomolybdate. The following procedure is the same as is given in the volumetric method following: The permanganate titration of the reduced molybdic acid divided into the amount of phosphorus known to be present in the solution will give the value of the permanganate in terms of phosphorus.

$$\frac{\text{Wt. of P in sample}}{\text{ml. } KMnO_4 \text{ required}} = \text{amount of P per ml. of } KMnO_4.$$

Method.—In a 400-ml. casserole dissolve 1 g. of the metal in 10 ml. of HNO_3, sp.gr. 1.42. Add 20 ml. of HCl, sp.gr. 1.20, and evaporate to dryness. Moisten with HCl, evaporate to dryness again, and bake to dull redness. Moisten with HCl again, and dilute to about 200 ml. with distilled water and filter if cloudy. To the solution add NH_4OH, sp.gr. 0.90, until the iron is entirely precipitated, and then add HNO_3, sp.gr. 1.42, cautiously until the solution just becomes clear, the solution having an amber color. Bring the solution to a temperature of about 80° C., and add 40 ml. of ammonium molybdate at room temperature. Allow to stand for one minute, shake or agitate for 3 minutes, filter on a 9-cm. paper, and wash very thoroughly (about 25 times) with acid ammonium sulfate. Dissolve the precipitate on the paper using 50 ml. of dilute ammonia. Add 10 ml. of H_2SO_4, sp.gr. 1.84, and immediately pass the solution through a Jones reductor, which has the reductor

tube prolonged and reaching nearly to the bottom of the flask, dipping into 50 ml. of ferric-alum solution.[7] Wash through the reductor with 150 ml. of distilled water, and follow with an additional 100 ml. of distilled water. Titrate with standard $KMnO_4$.

By this method the molybdenum in passing through the reductor is reduced entirely to the form Mo_2O_3, and is oxidized by the ferric alum to the form MoO_3, an equivalent amount of iron being reduced to the ferrous condition. As the yellow precipitate contains one atom of phosphorus to each twelve molecules of MoO_3, and as three atoms of oxygen oxidize two of molybdenum, eighteen oxygens or thirty-six irons are equivalent to one phosphorus. Therefore, the iron value of the permanganate multiplied by the factor $P/36 \times Fe$ (or 0.01540) gives the value of the permanganate in terms of phosphorus.

Accuracy.—Duplicate determinations should check within 0.005% of phosphorus.

NOTES.—The ammonium molybdate solution should be kept in a cool place and should always be filtered before using.

A blank determination should be made on corresponding amounts of acid and water, passing through the reductor into the usual amount of ferric-alum solution in the flask.

A small quantity of liquid should always be left in the reductor funnel, and air should never be allowed to enter the reductor.

Calculation. CASE 1.—If ferric sulfate is in the receiver ($6Mo_2O_3+18\ O = 12MoO_3$ in the molecule containing 1P), 18 O are equivalent to 36H, hence N/10 P according to this reaction equals at.wt. P divided by $(36 \times 1000) = P$ for 1 ml. of N/10 $KMnO_4 = .0000862$ g. P.

CASE 2.—No ferric salt in receiver. $Mo_{24}O_{37}+35\ O = 24MoO_3+2P \cdot (35\ O = 70H)$. Dividing by 2 we get at.wt. P divided by $(35 \times 1000) = P$ for 1 ml. of N/10 $KMnO_4 = .0000887$.

NOTES.—In case the alkalimetric method is chosen, it will be necessary to wash the precipitate free of acid by washing with neutral ammonium nitrate. (Washing with pure water is prohibited owing to the solubility of the precipitate.) A litmus paper test of the filtrate coming from the funnel is the usual practice of ascertaining whether this washing is complete. Sufficient time should be allowed for the standard alkali to react with the precipitate before addition of standard acid in the titration of the excess alkali, otherwise the results will be low; this is specially true if much "yellow precipitate" is present. If the permanganate method has been chosen, washing the precipitate with ammonium sulfate is the general practice, as the presence of nitrate salts in the precipitate would cause error in this reduction method.

As ammonium molybdate is apt to deteriorate after standing for several weeks, it is advisable to test the reagent before use. A fresh solution should be made up every ten or fifteen days.

In precipitating phosphorus it must be remembered that overheating the solution will cause the precipitation of molybdic oxide; should this be suspected, the magnesium phosphate method will correct results.

Special Steels and Alloys.—Steels containing titanium, tungsten, vanadium, etc., require a special treatment in preparing these for analysis, in the determination of phosphorus. Directions are given for these on the following page, 702.

Ferro-Silicon, Iron Phosphide and Acid-Insoluble Alloy Steels.—Decomposition is best accomplished by fusing 1–2 grams with 10–15 grams of a mixture of sodium carbonate and magnesium oxide (2 : 1). (A blank should be run on the reagents and allowance made for any phosphorus present.) The fusion is dissolved in hydrochloric acid, then taken to dryness and the SiO_2 filtered off. The SiO_2 is treated with HF and a few drops of H_2SO_4 in a platinum dish and taken to fumes. The residue is fused

[7] It is not required to heat the solution for reduction as is sometimes stated in text books.

with Na_2CO_3, and the fusion dissolved in HCl and the solution added to the main filtrate containing the iron and phosphate, etc. This filtrate is concentrated to near dryness, 10 ml. nitric acid added, and the evaporation repeated. This concentrate is diluted to about 25 ml. and phosphorus precipitated with ammonium molybdate solution as usual.

Ferro-Titanium, Metallic Titanium.—The fusion, obtained as directed for ferro-silicon, is extracted with water to dissolve out the sodium phosphate. The residue is fused with sodium carbonate and again extracted with water. The water extracts of the two fusions are examined for phosphorus. The extracts are made acid with nitric acid, the solution evaporated to near dryness, nitric acid added and the concentrated solution treated as directed for steel. Iron, in this case, has been removed with titanium.

Preparation of Cast Iron and Alloy Steels for the Determination of Phosphorus. *Cast Iron.*—One gram or more of the sample is dissolved in 50 ml. of dilute nitric acid, the solution evaporated to dryness and baked at 200° C. for an hour, 15 ml. of hydrochloric acid (sp.gr. 1.2) are added and the solution again evaporated to dryness. Fifteen ml. hydrochloric acid are added to the residue, 20–30 ml. of water, and the silica is filtered off and washed with water.[8] The filtrate is evaporated to pasty consistency, 15 ml. of nitric acid are added and the solution evaporated to near dryness, this treatment is repeated and the residue then taken up with 15 ml. of water. Phosphorus is now precipitated according to the directions for phosphorus in the steel solution.

Iron Containing Titanium.—The material is treated as in case of cast iron. Any residue remaining from the nitric acid evaporation is treated with HF and H_2SO_4 as in case of cast iron. (Use platinum dish.) The residue remaining from the HF treatment is taken up with a little HCl and filtered. The filtrate being added to the main solution containing iron and phosphorus. The solution is heated to boiling and an ammonium acid sulfite solution is added, dropwise (2 ml. of NH_4OH saturated with SO_2 and 10 ml. NH_4OH). A precipitate will form, which dissolves. In case it does not, on stirring, the solution is cleared by adding a few drops of HCl, and the addition of sulfite continued. When all but 1–2 ml. of the reagent is added, the solution is heated. Ammonium hydroxide is now added drop by drop to the hot solution until a slight greenish precipitate is formed in the solution, which remains undissolved on stirring. Now the remaining 1–2 ml. of the sulfite is added. If a precipitate forms (titanium hydroxide) which does not redissolve on stirring, HCl is added drop by drop until the solution clears. The odor of SO_2 should be evident. If not, more sulfite should be added and the solution again cleared. Five ml. HCl are added, CO_2 passed through the solution, which is heated to boiling to expel excess of SO_2, the iron remaining in the reduced form. Sufficient ferric chloride is now added to combine with all the phosphorus and a slight excess.

The solution is cooled under tap water and ammonium hydroxide added drop by drop until green ferrous iron precipitate redissolves, and then a white precipitate of titanium hydroxide and ferric phosphate remains and an additional drop causes a distinct reddish tint and the appearance of a green precipitate with one more. If the red color does not appear, the green precipitate is dissolved with a few drops of HCl and additional ferric chloride solution is added. The addition of ammonia is now repeated. A reddish color of excess of ferric hydroxide should be evident.

[8] Traces of P in residue are recovered by treating with HF and H_2SO_4 and expelling SiO_2.

A few drops of acetic acid (sp.gr. 1.04) are added to dissolve the green precipitate, the red remaining undissolved, and 1 ml. excess. The solution is diluted to about 450 ml. with hot water, boiled 1 minute, then rapidly filtered, and washed once or twice with hot water. The filtrate passes through clear, but will become cloudy upon oxidation of iron.

The residue is dried, separated from the filter, the latter burned and its ash added to the main residue. This is mixed with 5 grams of sodium carbonate and about 0.2 g. potassium nitrate and fused in a platinum crucible for half an hour. The fusion is extracted with water and the solution filtered. The filtrate contains all the phosphorus as sodium phosphate.

The filtrate is acidified with nitric acid and evaporated to near dryness, then taken up with a few ml. of water and to a volume of 25 ml. is added the ammonium molybdate solution according to the procedure for iron and steel. The procedure from this stage is the same as for steel.

Vanadium Steels.—In presence of vanadium the ammonium phosphomolybdate will be contaminated with vanadium, so that its presence requires a special treatment. If less than 2.5% is present, the regular procedure for steel is followed with the exception that just before adding the ammonium molybdate, 5–10 ml. nitric acid are added.

If more than 2.5% of vanadium is present, the following procedure is recommended by C. M. Johnson (J. Ind. Eng. Chem., 11, 113, 1919): 1 gram of steel is treated in a covered 250-ml. porcelain dish with a mixture of 30 ml. concentrated hydrochloric acid and 30 ml. concentrated nitric acid, and the solution is heated for an hour. The cover is rinsed off into the main solution, 100 ml. of strong nitric acid is added and the solution evaporated to dryness and baked for 5 minutes at 200° C. The oxides are dissolved in 35 ml. of concentrated hydrochloric acid and the solution evaporated to about 10 ml. Ten ml. of nitric acid are added and the covered solution heated for a few minutes. The solution is filtered through asbestos, on a small wad of glass wool in a funnel. The vanadium oxide residue is washed 15 times with small portions of a solution containing 200 ml. concentrated nitric acid, 100 ml. water and 20 grams of ferric nitrate (free from phosphorus). The filtrate is concentrated to 10 ml. If a precipitate forms V_2O_4, it is filtered off and the washing repeated, the filtrate is again evaporated and filtered if necessary. If no precipitation occurs in the filtrate upon concentration, 40 ml. of nitric acid are added and the phosphorus precipitated with ammonium molybdate [9] as usual.

NOTE.—Vanadium may also be precipitated by concentration to about 20 ml., neutralizing the greater part of the acid and adding ammonium chloride solid to saturation. The precipitate is washed with a saturated solution of NH_4Cl.

ANALYSIS OF TRI-SODIUM PHOSPHATE [10]

1. SAMPLING

Each sample shall consist of at least two pounds of material taken in the following manner: Employ a sampler that removes a core from the container

[9] Johnson recommends ammonium molybdate that contains 55 grams of ammonium molybdate, 50 grams of ammonium nitrate, 40 ml. ammonium hydroxide, and 700 ml. water. After heating for half an hour, the solution is diluted to 1000 ml. The solution is allowed to settle for 24 hours and is filtered. It is slightly ammoniacal.

[10] By courtesy of the American Cyanamid Company.

from top to bottom. Take cores of each barrel or bag comprising the shipment, and place each sample in the container provided for that purpose. The container should be kept closed except during the introduction of the sample. Thoroughly mix the portions, and reduce by quartering to about two pounds and place in an air-tight container.

2. Color and Crystal Form

Examine the sample for color and crystal form by comparison with the "Master Batch."

3. Moisture

Heat twenty grams of the crystals for one hour at 105° C. Cool in a dessicator and weigh. Grind this dried sample rapidly in a mortar. Ignite three grams of the powder at a dull red heat. Cool, weigh and calculate the total water content of the material. Subtract from this value the theoretical amount of moisture calculated as the $12H_2O$ salt, equivalent to the sodium phosphate content as determined in paragraph 5, and report the amount of free moisture.

4. Screen Size

Set up the following screens with a top and bottom section: 10, 20, and 100 mesh (U. S. Standard Specifications for Sieves). Place fifty grams of material on the 10 mesh screen, and then place the nest of screens in the Ro-Tap machine and agitate for fifteen minutes. Brush the quantity left on each screen carefully upon a balanced watch-glass and weigh. Report the results in per cent through each screen.

5. Total Sodium Phosphate

A. Reagents.—Prepare the reagents as directed on p. 697.

B. Determination.—Weigh a two-gram sample into a 200-ml. volumetric flask, and add 50 ml. of water. Boil the solution gently for thirty minutes. Cool to room temperature and make up to the mark with water. Filter the solution through a dry paper discarding the first 15 ml. Draw off a portion of the filtered solution by means of a pipette which has been standardized to deliver one-eighth of the contents of the flask and run it into a 400-ml. tall form beaker containing 25 ml. of water. Add 25 ml. of concentrated ammonium hydroxide and then just acidify by careful addition of concentrated nitric acid. The end-point may be determined by the use of litmus paper which must then be washed off and removed from the solution. The temperature of the solution should now be about 55° C. (heat of neutralization). Place the beaker in a water bath regulated at 55° C. Add 85 ml. of the molybdate solution drop by drop from a burette, stirring the solution continuously with a mechanical device if available. The addition of the molybdate solution shall be at such a rate as to require five minutes for its completion. Stir the solution by hand occasionally for another five minutes and then allow to stand in the bath for five minutes longer to settle the precipitate. Filter the precipitates by suction on a previously dried and weighed Gooch crucible. Decant the clear liquor first and stir up the precipitate with 25 ml. of 1% nitric acid

and then wash it completely into the crucible. Wash the precipitate by filling the Gooch five times with the 1% nitric acid. Finally fill the Gooch with distilled water and suck the precipitate as dry as possible. Heat the crucible in an oven at 115° C. for two hours. Weigh the "yellow precipitate" and convert it to P_2O_5 by multiplying the factor 0.03784. Calculate the percentage of total phosphoric acid, P_2O_5, on the "original" moisture basis.

6. Insoluble Material

Dissolve fifty grams of the material in 300 ml. of hot water and filter off the insoluble matter on a weighed Gooch crucible. Wash the residue thoroughly with hot water and save the filtrate for the determination of sulfate, chloride, and total alkalinity. Dry the crucible in an oven at 105° C. and weigh. Calculate the per cent of *insoluble*.

7. Total Alkalinity

Add sufficient water to the filtrate saved from the determination of *insoluble*, to make the volume exactly 500 ml. Titrate 25 ml. of this solution with one-half normal (0.5 N) hydrochloric acid, using methyl orange as the indicator. Calculate the per cent Na_2O from the number of milliliters of hydrochloric acid used.

8. Total Sodium Sulfate

Add a 100-ml. portion of the solution prepared for the determination of *Total Alkalinity* to 100 ml. of water containing 5 ml. of concentrated hydrochloric acid and determine the sulfate content by precipitation with barium chloride. Calculate the per cent of Na_2SO_4 from the weight of barium sulfate obtained.

9. Total Sodium Chloride

A. Reagents.—1. ***Standard Silver Nitrate Solution.***—Dissolve seventeen grams of silver nitrate in water, filter and dilute the filtrate to one liter.

2. ***Standard Ammonium Thiocyanate Solution.***—Dissolve seven and six-tenths grams of ammonium thiocyanate in approximately 100 ml. of water, filter, and dilute to one liter.

3. ***Ferric Ammonium Sulfate Solution.***—Saturate 100 ml. of distilled water with ferric ammonium sulfate, at room temperature (20° C.). Filter, and add just enough nitric acid to remove the turbidity and change the color from red to pale yellow.

4. ***Potassium Chromate Solution.***—Prepare a saturated solution of the C. P. salt in distilled water.

B. Standardization of Reagents.—1. ***Standard Silver Nitrate Solution.***—Weigh accurately two-tenths of a gram of pure sodium chloride, previously dried at 105° C. for one hour, and dissolve it in 50 ml. of distilled water. Add two drops of potassium chromate indicator and titrate with the silver nitrate solution to the appearance of a brown coloration. Calculate the amount of silver nitrate equivalent to the sodium chloride and then calculate the normality of the standard solution.

2. ***Standard Ammonium Thiocyanate Solution.***—Measure accurately from a burette, 35 ml. of the standard silver nitrate solution, add 2 ml. of concentrated nitric acid, and dilute to 150 ml. with distilled water. Titrate with the ammonium thiocyanate solution, using 1 ml. of the ferric ammonium sulfate indicator. Calculate the volume of the ammonium thiocyanate solution equivalent to 1 ml. of the standard silver nitrate solution.

C. Determination.—Remove a 200 ml. portion of the solution prepared for the determination of sulfate and acidulate it with nitric acid, adding 2 ml. in excess. Add 15 ml. of the standard silver nitrate solution. Filter and wash the precipitate. Titrate the excess silver nitrate with the standard ammonium thiocyanate solution using the ferric ammonium sulfate indicator, and calculate the per cent of NaCl in the sample.

DETERMINATION OF PHOSPHORUS IN PRESENCE OF VANADIUM [11]

The exact determination of phosphorus in the presence of large amounts of vanadium is an exceedingly difficult matter. The Zirconium Method, which is accurate and simple, is recommended for general use.

1. Zirconium Method

Note.—This method may be used most satisfactorily for the determination of phosphorus in lead molybdate, wulfenite ores.

One gram, or if the phosphorus content of the ore is less than 0.10%, two grams, of the 100-mesh ore is treated with 50 ml. of hydrochloric acid (sp.gr. 1.19) in a 600 ml. beaker provided with a clock-glass cover and the contents of the beaker are heated at a temperature of about 60° C. When the reaction appears to be complete, the volume of the liquid is reduced by evaporation to approximately 30 ml., fifty milligrams of zirconium in the form of zirconium chloride and 5 ml. of hydrobromic acid (sp.gr. 1.38) are added and the solution is evaporated to dryness and baked to decompose chlorides. The evaporation with hydrobromic acid results in the volatilization of any *arsenic*.

Sixty ml. of hydrochloric acid (1 : 1) are added and the beaker and its contents are heated until the residue has largely dissolved when the liquid is boiled down to a volume of about 25 ml. Five hundred ml. of boiling water and a considerable amount of ashless paper pulp are added and the solution is digested for about one-half an hour at a temperature of approximately 60° C. The solution is then filtered hot and the precipitate, which will contain all of the phosphorus (in the form of zirconium phosphate), together with silica, etc., is filtered on an 11 cm. paper and washed thoroughly with *hot* 0.5% hydrochloric acid to remove lead, vanadium, iron, copper, zinc, etc., the filtrate and washings being discarded.

The precipitate of zirconium phosphate, silica, etc., is ignited in a porcelain crucible at a *dull red heat* (no higher) until the carbon of the filter paper has been destroyed, transferred to a large platinum crucible and treated with approximately 2 ml. of nitric acid (sp.gr. 1.42) and 5 ml. of hydrofluoric acid (48%). The solution is slowly evaporated nearly to dryness. If much quartz is present, it will be necessary to repeat the treatment with nitric and hydrofluoric acids in order to effect its complete removal. One ml. of sulfuric acid (1 : 1) is then

[11] Method of the Electro-Metallurgical Company. By courtesy of T. R. Cunningham.

added and the evaporation is continued until fumes of sulfur trioxide are no longer evolved. The residue should not be ignited.

The precipitate of zirconium phosphate (from which the silica has been separated as described in the preceding paragraph) is fused with from five to ten grams of sodium carbonate and the fused mass is extracted with hot water. When the melt has disintegrated the crucible is removed from the solution and rinsed with a jet of water. The liquid is boiled for several minutes with the occasional addition of a small amount of sodium peroxide. The contents of the beaker are then filtered on a 9-cm. paper and the residue of sodium zirconate is washed thoroughly with a hot 2% solution of sodium carbonate. If the zirconium phosphate has not been heated at an unnecessarily high temperature in any of the preceding operations the fusion with sodium carbonate will completely decompose it into sodium phosphate and sodium zirconate, the former of which will pass quantitatively into the filtrate, whereas the latter will all remain on the paper.

The filtrate and washings from the sodium zirconate are acidified with sulfuric acid (1 : 1), and boiled to expel carbon dioxide. Ten (10) ml. of a 2% solution of ferric sulfate (free from phosphorus) and a slight excess of ammonium hydroxide are added, the solution is heated to boiling, and the ferric hydroxide, which will carry down all of the phosphorus, is filtered on a 9 cm. paper and washed with hot water to remove all sodium salts.

The precipitate of ferric hydroxide is dissolved off of the paper in 20 ml. of hot nitric acid (1 : 1), and the filtrate and washings, which should have a combined volume of not more than 75 ml., are collected in a 300 ml. Erlenmeyer flask. Five (5) grams of ammonium nitrate are added and the temperature of the solution is brought to 25° C. Approximately 0.2 gram of ferrous sulfate (free from phosphorus) and 60 ml. of "molybdate solution" are then introduced and the phosphorus is precipitated as ammonium phosphomolybdate by *five minutes vigorous shaking*. By precipitating the phosphorus with "molybdate solution" at 25° C., arsenic, if present, will not interfere. This temperature must be strictly adhered to. The precipitate is allowed to settle and the determination of the phosphorus is completed by either the Alkalimetric or the Molybdenum Reduction (Emmerton) Method. A "blank" is run on all of the reagents and deducted.

REFERENCE

Report by the Committee on Research and Analytical Methods—Phosphate Rock, J. Ind. Eng. Chem., 7, 446 (1915).

THE VOLUMETRIC ESTIMATION OF SMALL AMOUNTS OF PHOSPHORUS, USING A STANDARD SOLUTION OF METHYLENE BLUE [12]

An oxidimetric process for the estimation of small amounts of phosphorus has been satisfactorily worked out, which depends upon the formation of the ammonium phosphomolybdate precipitate, solution of this in ammonium hydroxide, reduction to molybdenum trichloride by hydrochloric acid and zinc in an air-free atmosphere and titration to molybdenum pentachloride with a standard solution of methylene blue, on the assumption that the ammonium phosphomolybdate has the normal composition, $(NH_4)_3PO_4 \cdot 12MoO_3 + nH_2O$.

[12] By courtesy of William M. Thornton, Jr. and H. L. Elderdice, Jr., J. Am. Chem. Soc., 45, 668 (1923).

Procedure.—The amount of phosphorus should not exceed 0.0004 g. (corresponding to 0.015 g. of molybdenum).

Standard solutions of the dye are prepared by dissolving "medicinal" methylene blue in water, filtering and adding more water until the requisite concentration had been reached, 4 g. to the liter being a suitable strength for most purposes. Standardization is then effected by titrating measured portions, acidified with hydrochloric acid and kept hot, with a known solution of titanous sulfate in an atmosphere of carbon dioxide. The titer of the titanous sulfate solution should be previously established either by means of specially prepared ferrous ammonium sulfate or indirectly with certified sodium oxalate from the Bureau of Standards.

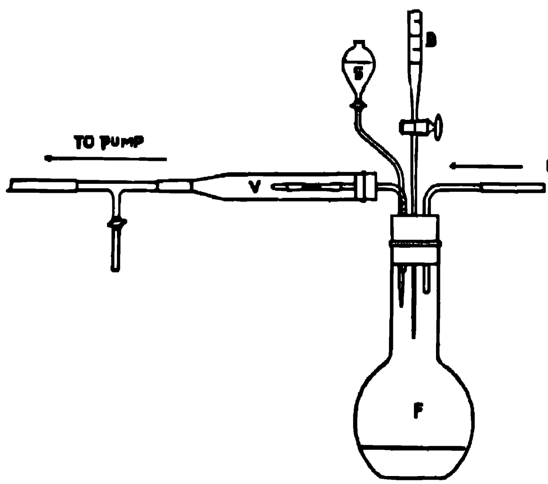


FIG. 87.—Apparatus for the Determination of Phosphorus.

The assay is placed in the Johnson sulfur flask *F* of 275 ml. capacity, which was fitted with a 4-hole rubber stopper containing inlet and outlet tubes, dropping funnel and burette tip. The exit tube is terminated by a Bunsen valve *V*, and this is enclosed in a larger tube tapering at the forward end and leading eventually to the pump, the intervening *T*-tube with stopcock being intended to permit relieving the suction without changing the rate of flow of water through the pump. Five g. of 30-mesh zinc having been introduced into the flask, the suction is turned on and continued throughout the reduction; after 2 to 3 minutes has elapsed, carbon dioxide from a Kipp generator (not shown in the figure) is passed through the flask for 10 minutes, thus removing practically all air from within the system. About 50 ml. of hydrochloric acid (d., 1.18) is then admitted from the tap funnel *S*, *very slowly*, so that the reduction proceeds at a moderate rate to completion. As soon as vigorous action has ceased, the solution is boiled to dissolve all remaining zinc, only a few seconds being required, whereupon the titration is accomplished with standard methylene blue already contained in the burette *B*. The following color changes are observed: salmon-pink to light yellow, light yellow to light green and finally light green to dark green—the last transformation from light to dark green on

the further addition of a drop of methylene blue denoting the point of complete reaction.

In case aliquot parts were to be taken, the entire ammoniacal solution of the yellow precipitate was transferred to a 50 ml. volumetric flask and the solution made up to the mark with water; otherwise, the filtrate and washings were caught directly in the Johnson flask. In dealing with low-phosphorus steel, wherein the division of the test solution proved unnecessary, it was found desirable to increase somewhat the amounts of zinc and hydrochloric acid to insure a complete reduction in the greater volume; accordingly, about 7 g. of the former and 65 ml. of the latter were used. Ordinarily, however, several 10 ml. portions were taken; and, from this point on, the procedure followed was exactly like that described above.

ELEMENTS OF THE PLATINUM GROUP
PLATINUM, PALLADIUM, IRIDIUM, RUTHENIUM, RHODIUM, OSMIUM[1]

The members of the platinum group—platinum, palladium, iridium, rhodium, ruthenium and osmium—occur in nature in alloyed form chiefly in the metallic state with the base metals copper and iron, and sometimes with native gold. However, platinum arsenide and ruthenium and osmium sulfides are found in nature but these are rare. The mineral sperrylite, platinum arsenide $PtAs_2$, has a tin-white metallic luster and is found in the nickel ores of Sudbury, Ontario, Canada. The mineral laurite, ruthenium sulfide Ru_2S_3, has a metallic luster and is found in the platinum washings of Borneo. Platinum deposits of commercial importance occur in the Ural Mountains, British Columbia, and South America.

The assay method by fusion with a litharge flux, similar to the method for gold and silver ores, is used in evaluation of the original ores. Analysis, however, generally deals with concentrates, alloys, jewelers' sweeps, pen-point material, scrap, catalyst masses, etc. A very large amount of alloy in which ruthenium and osmium predominate has replaced the original osmiridium grains for tipping fountain pen-points.

The entire group of platinum metals can be brought into solution by fusing with a mixture of barium peroxide and barium nitrate, and extracting with dilute hydrochloric acid.

Hydrogen sulfide precipitates all metals from hot solutions with a hydrochloric acid content up to about five percent; iridium solutions should have about twenty percent hydrochloric acid. Platinum from platinum ammines cannot be completely precipitated by hydrogen sulfide or ammonium chloride. All sulfides are soluble in aqua regia. The sulfides of palladium, rhodium and osmium are insoluble in ammonium sulfide, whereas, the sulfides of iridium, platinum and ruthenium are soluble, the latter two with difficulty. The ignition of the sulfides yields metal in the case of platinum, oxidized residues with ruthenium, iridium, rhodium, palladium, and the volatile tetroxide with osmium. Some sulfur will be retained in all cases.

Concentrated sulfuric acid will attack palladium and finely divided osmium, but less so than nitric acid. In both cases the osmium goes off as the tetroxide.

When the metals are alloyed with lead and dissolved in dilute nitric acid, some rhodium and platinum will go into solution with the lead, and by treating the wet residue with dilute aqua regia or concentrated sulfuric acid, the remaining rhodium and platinum will dissolve leaving the iridium insoluble. These treatments provide a clean separation of iridium and rhodium.

Mercuric cyanide, $Hg(CN)_2$, gives a white precipitate of palladium cyanide, $Pd(CN)_2$, while the other metals are not affected.

[1] **Chapter by R. E. Hickman.**

Chlorine will distill ruthenium and osmium at the same time from ruthenate and osmate solutions; nitric acid will distill osmium only. Care should be taken not to have the solution too strong with nitric acid as there is a tendency for a small amount of ruthenium to be carried over. Organic matter should not be present when osmium is distilled with nitric acid.

Zinc will precipitate all metals from the chloride solutions, iridium being very difficult to precipitate completely. The precipitates will always contain a small amount of zinc. Magnesium and aluminum are somewhat cleaner.

PLATINUM

Pt, *at.wt.* 195.23; *sp.gr.* 21.48; *m.p.* 1755° C.; *oxides* PtO, PtO_2

DETECTION

Platinum is a gray, lustrous, soft and malleable metal. It is not altered by ignition in the air, but fuses in the oxy-hydrogen flame. It does not dissolve in any of the single acids, but a fusion with acid potassium sulfate attacks the metal slightly. The action of chlorine in general, and nitro-hydrochloric acid (aqua regia), the main solvent, converts the metal to hydrochlorplatinic acid, H_2PtCl_6, which forms many double salts, or platinichlorides. If platinic chloride is gently heated it breaks up into platinous chloride, $PtCl_2$, and chlorine.

If, however, the platinum is alloyed with silver, it dissolves in nitric acid to a yellow liquid, provided sufficient silver is present in the alloy.

The oxides can be formed by carefully igniting the corresponding hydroxides. These are very unstable, decomposing into metal and oxygen by gentle ignition.

The chlorides are the most important compounds of platinum. Two complex acids are formed with hydrochloric acid when the metal is dissolved in aqua regia.

$PtCl_4 + 2HCl = H_2PtCl_6$ (chloroplatinic acid), orange-red crystals.

$PtCl_2 + 2HCl = H_2PtCl_4$ (chloroplatinous acid), only known in solution.

An aqueous solution of the former is yellowish-orange, while an aqueous solution of the latter is dark brown, the former being by far the more important.

Potassium iodide precipitates platinum iodide, but it dissolves quite readily, giving a pink to a dark blood-red liquid, depending on the concentration of the solution. Nitric acid should be absent. Heat destroys this color, as well as hydrogen sulfide, sodium thiosulfate and sulfite, sulfurous acid, mercuric chloride and certain other reducing reagents.

Hydrogen sulfide precipitates black platinum disulfide, PtS_2, with the other elements of the hydrogen sulfide group. The solution should be hot, as precipitation takes place more quickly. It is difficultly soluble in ammonium sulfide. It will be found in the extract with the arsenic, antimony, tin, gold, molybdenum, etc., and is precipitated with these elements upon addition of hydrochloric acid. Platinum sulfide is soluble in aqua regia. Addition of $MgCl_2$ solution prevents formation of colloidal PtS_2.

Ammonium chloride added to a concentrated solution of platinum chloride precipitates yellow $(NH_4)_2PtCl_6$, which is slightly soluble in water, and less so in dilute ammonium chloride solution and alcohol.

Potassium chloride precipitates yellow K_2PtCl_6, which is slightly soluble in water, but insoluble in 75% alcohol.

Ferrous sulfate precipitates metallic platinum on boiling from a neutral solution. Neutralize with Na_2CO_3. Free mineral acids (except dilute H_2SO_4) prevent the precipitation (difference from gold).

Stannous chloride does not reduce platinum chloride to metal, but reduces hydrochlorplatinic acid to hydrochlorplatinous acid.

$$H_2PtCl_6+SnCl_2=H_2PtCl_4+SnCl_4.$$

Oxalic acid does not precipitate platinum (difference from gold).

Sodium hydroxide with glycerine reduces hydrochlorplatinic acid on warming to black metallic powder.

Formic acid precipitates from neutral boiling solutions all the platinum as a black metallic powder.

Thallium protoxide precipitates from the platinum bichloride solution a pale yellow salt, thallium platinochloride. When the salt is heated to redness it leaves an alloy of thallium and platinum.

Sodium hydroxide added to platinic chloride and then acidified with acetic acid produces a pale yellow to orange precipitate of platinic hydroxide, $Pt(OH)_4$. This dissolves in acids readily, except acetic acid.

Metallic zinc, magnesium, iron, aluminum and copper are the most important metals that precipitate metallic platinum.

$$H_2PtCl_6+3Zn=3ZnCl_2+H_2+Pt.$$

ESTIMATION

Platinum may be present under the following conditions:

1. Native grains usually accompanied by the other so-called platinum metals, iridium, palladium, ruthenium, rhodium, osmium, and gold and silver (alloyed with one or more of the allied metals).

Ore concentrates containing the native grains as above with the base metals, iron, copper, chromium, titanium, etc. The associated minerals high in specific gravity in the gravels may be expected to appear with the platinum nuggets, such as chromite, magnetite, garnet, zircon, rutile, small diamonds, topaz, quartz, cassiterite, pyrite, epidote, and serpentine; with gold in syenite; ores of lead and silver.

2. Scrap platinum containing, oftentimes, palladium, iridium, gold, silver and iron.

3. Small amounts of platinum in the presence of large amounts of iron, silica, carbon, magnesia: platinum residues, nickel and platinum contacts, photographic paper, jewelers' filings and trimmings, dental and jewelers' sweeps and asbestos, etc.

4. Platinum alloyed with silver, gold, tungsten, nickel, copper, lead, etc.
5. Platinum solutions and salts.

PREPARATION AND SOLUTION OF THE SAMPLE

The best solvent for platinum is aqua regia. The metal is also acted upon by fusion with the fixed alkalies—sodium or potassium hydroxide and sodium peroxide or potassium or sodium nitrate; also by chlorates in the presence of HCl. Platinum, when highly heated, alloys with other metals, as lead, tin, bismuth, antimony, silver, gold, copper, etc. The element dissolves in nitric acid when alloyed with silver. This gives a method for the determination of gold in the presence of silver and platinum alloy.

All salts of platinum are soluble in water. The less soluble salts are the chloroplatinates of potassium, ammonium, rubidium, and caesium. Heat increases the solubility while the presence of alcohol decreases the solubility.

Ores.—When the free grains of platinum, gold and osmiridium are desired the following method is recommended: Five to 10 grams of the ore are taken from a well-mixed pulverized sample and placed in a large platinum dish. Twenty-five to 50 ml. of strong hydrofluoric acid together with 5 to 10 ml. of concentrated sulfuric acid is mixed with the ore in the dish and evaporated on the water bath, when SiF_4 and the excess of HF are expelled. The material is gently heated until SO_3 fumes are given off. This is repeated with HF if necessary. The material is washed into a casserole with about 200 ml. of hot water and digested over a water bath for fifteen or twenty minutes, and is then washed by decantation, several times pouring the supernatant liquor through a filter to save any floating material that might be washed out. The filter is cautiously burned and the residue is added to the unattacked material. This is treated with aqua regia and filtered. The platinum and a small amount of iridium that dissolves with the platinum on account of its being alloyed can be precipitated with ammonium chloride. The residue is cautiously ignited and treated with HF and H_2SO_4 in a platinum dish as described above. After washing and drying the bright grains are weighed as osmiridium. The sand and osmiridium can also be fused with silver and borax, then extracted with dilute nitric acid, leaving the osmiridium grains free from sand.

Platinum Scrap.—One-half gram to a gram is dissolved in aqua regia and evaporated with HCl to get rid of the HNO_3.

If the platinum is alloyed with a large amount of copper, silver, lead and other impurities, a sample of 1 to 5 grams is dissolved in 15 to 25 ml. of HNO_3, whereby the copper, silver, lead and other impurities alloyed with the platinum as well as a large amount of platinum will dissolve. The residue after washing

will be platinum and gold. These are dissolved in aqua regia as described above and the platinum precipitated with ammonium chloride. The platinum is recovered from the nitric acid solution and added to the aqua regia solution and the whole is evaporated to get rid of the HNO_3.

Small Amounts of Platinum in the Presence of Large Amounts of Iron; Iron Scale, Fe_2O_3; Sulfate of Iron, Magnesia, Sulfate of Magnesia, Silica, etc.—The material is carefully weighed and the coarse scales are separated from the finer material containing the platinum by passing the fines through a 20-in. mesh or finer wire sieve. The coarse scale seldom contains platinum, but it is advisable to quarter this down to 1 kilogram or a fairly good-sized sample and test for platinum on a portion of the ground sample. This can be tested by a wet or a fire assay. The fines are quartered down to about 1 kilogram and ground to pass a 60- to 80-in. mesh sieve. One hundred to 500 grams of the material are taken for analysis. This is placed in one or more casseroles, depending on the amount taken. Each 100-gram portion is extracted by digestion on the steam-bath with about 300 to 400 ml. of 10% H_2SO_4. The iron, magnesia, etc., soluble in H_2SO_4 will go into solution, leaving the platinum with the insoluble residue. Filter (a Büchner funnel may be necessary) and wash the residue with water. Test the filtrate for platinum and if any is present precipitate with zinc as described below.

After the filter is ignited in a large platinum dish, the residue is moistened with H_2SO_4, and HF is added completely covering the material. The solution is evaporated on the water bath until SO_3 fumes are given off. If necessary, repeat the treatment with H_2SO_4 and HF until all the silica is driven off as SiF_4. The residue is transferred to a casserole and digested with aqua regia according to directions given under Ores and Platinum Scrap. It is sometimes very difficult to precipitate all of the platinum in the presence of a large amount of iron, magnesia, etc., not having the solution concentrated enough for the platinum. It is advisable to reduce the platinum by iron or zinc, filter, wash with water and redissolve the black metallic platinum in aqua regia. The HNO_3 is expelled by evaporation and adding concentrated HCl from time to time and finally the platinum is precipitated with ammonium chloride.

SEPARATIONS

A careful review of the paragraphs on Detection will be very helpful oftentimes in making separations from other metals and substances.

Separation of Platinum from Gold.—(1) The platinum is precipitated first with ammonium chloride, as $(NH_4)_2PtCl_6$. After the precipitate has settled it is filtered and washed free from gold with 20% ammonium chloride solution and

alcohol. The gold is precipitated with a concentrated solution of ferrous sulfate or chloride as metallic gold. (See also page 434.)

(2) Oxalic acid precipitates gold, leaving the platinum in solution. The oxalic acid is added and the solution heated until the gold is entirely precipitated. Filter and wash the precipitate of metallic gold free from platinum. The filtrate is evaporated as far as possible without crystallizing, and the platinum is precipitated with ammonium chloride as $(NH_4)_2PtCl_6$, or it may be reduced with zinc and the black dissolved in aqua regia and treated as described above.

Separation of Platinum from Iridium.—The platinum and the iridium are precipitated by iron or zinc and the black residue is washed free from impurities and the platinum is dissolved in dilute aqua regia with gentle heating, leaving the iridium as metallic iridium. The platinum solution is evaporated as described above and precipitated with NH_4Cl as $(NH_4)_2PtCl_6$.

If the platinum and iridium are precipitated together, the salt is filtered and washed with ammonium chloride solution and finally ignited. The sponge is redissolved and evaporated as above to expel the HNO_3. The platinum and the iridium are precipitated with NaOH, which brings down the platinum and iridium as $Pt(OH)_4$ and $Ir(OH)_4$. Boil this mixture with alcohol, which reduces the $Ir(OH)_4$ to $Ir(OH)_3$, but does not affect the $Pt(OH)_4$. Dissolve these hydroxides in HCl, forming $PtCl_4$ and $IrCl_3$ in solution, and the platinum is precipitated with NH_4Cl free from iridium.

See Deville-Stas-Gilchrist method on page 733, also Separations on page 731.

Separation of Platinum from Palladium.—Platinum is precipitated with ammonium chloride, and palladium is precipitated from the filtrate by means of dimethylglyoxime (1% alcoholic solution).

Palladium may be precipitated in presence of platinum by adding a 1% solution of dimethylglyoxime (1% salt in 95% alcohol) to the cold, slightly acid chloride solution of the elements. If the solution is hot the palladium precipitate will be badly contaminated with platinum.

Separation of Platinum from Ruthenium.—From the chloride solution of platinum and ruthenium the metals are precipitated with ammonium or potassium chloride and filtered. The filter is washed with dilute ammonium chloride solution and alcohol until free from ruthenium. If a large quantity is handled it may be necessary to ignite to platinum sponge and dissolve in aqua regia, expel the HNO_3 as described above, and reprecipitate with NH_4Cl, filter and wash free from ruthenium. (See also page 738.)

Separation of Platinum from Rhodium.—The separation is accomplished by adding freshly precipitated barium carbonate to the chloride solution of platinum and rhodium, previously brought nearly to the neutral point by addition of sodium hydroxide. After boiling for two or three minutes rhodium hydroxide precipitates. The precipitate is filtered off, dissolved in HCl, the solution again nearly neutralized and the rhodium precipitation repeated.

Other platinum metals will also precipitate if present. These should be removed prior to the separation of platinum and rhodium. (E. Wichers.) See Rhodium.

Separation of Platinum from Osmium.—Both metals are reduced with zinc as a fine black powder. The metallic residue is washed and carefully ignited at a high temperature under a hood, as the fumes are poisonous and

disagreeable like chlorine. The osmium will be converted into OsO_4, which is very volatile. The residue is dissolved in aqua regia and the platinum is precipitated with NH_4Cl. See Osmium.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF PLATINUM

A. WEIGHING AS METALLIC PLATINUM

1. When the platinum contains only a small amount of impurities a sample of 1/10 gram or more is taken and dissolved in aqua regia. The solution is gently heated until all is dissolved, adding another portion of aqua regia if necessary. The solution is evaporated, adding HCl from time to time in order to expel the HNO_3. Filter and evaporate again to concentrate the solution. Precipitate with ammonium chloride. After stirring, let stand until the precipitate, $(NH_4)_2PtCl_6$, settles, overnight if convenient. Filter, wash with alcohol or ammonium chloride solution and alcohol, and ignite to metal very slowly. Cool in a desiccator and weigh as metallic platinum.

$$\frac{\text{Wt. of Pt found}}{\text{Wt. of sample taken}} \times 100 = \text{per cent of Pt in the material.}$$

2. When the platinum solution contains a large amount of impurities, as iron, nickel, magnesia, etc., it is advisable to reduce the platinum to black metallic platinum with zinc, iron or magnesium as follows: The solution is made acid (2 to 5% free HCl) by adding HCl. The Zn, Fe or Mg is added in small quantities at a time until the solution becomes colorless or until the platinum is completely precipitated.[2] After action has ceased the platinum black metal is filtered onto an ashless filter paper and washed with warm dilute HCl to remove any excess Zn, Fe, or Mg that might be present. The filter and its contents are carefully ignited and afterwards dissolved in aqua regia and treated as directed under A, 1.

3. If none of the other Hydrogen Sulfide Group metals is present the platinum can be precipitated by hydrogen sulfide, filtered, washed with hot water and ignited to metal.[3] If impurities are present in the sulfide, dissolve in aqua regia and proceed as under A, 1. The solution should be boiling and have an acidity of 3% HCl or H_2SO_4.

[2] $FeCl_3$ in presence of HCl has a solvent action on platinum, hence the iron should be completely reduced.

[3] The ignition should be finished at a high temperature as it is very difficult to get rid of all the sulfur.

4. After distilling off the osmium and ruthenium as described under these metals, the solution containing the other platinum metals in the distilling flask is transferred to a liter beaker. HCl is added cautiously and the contents evaporated several times with additional HCl. If the flask is stained by IrO_2, clean it by adding 5 to 10 ml. of aqua regia and evaporate several times with HCl to get rid of the HNO_3. Add this to the main solution and evaporate it as far as possible on the steam-bath and then dilute to 200 ml. with water.

Heat the solution containing platinum, palladium, rhodium and iridium to boiling, and add to it 20 ml. of a filtered 10% solution of sodium bromate. Carefully add a filtered 10% solution of sodium bicarbonate until the dark green solution shows evidence of the formation of a permanent precipitate. Test the acidity of the hot solution from time to time by allowing a drop of brom cresol purple indicator solution (0.01%) to run down the stirring rod into the drop which clings to it as it is lifted from the solution. Enough bicarbonate has been added when the color of the indicator changes from yellow to blue. At this stage, add 10 ml. more of the bromate reagent and boil the solution for five minutes. Increase the pH of the solution slightly by carefully adding dropwise bicarbonate solution until a faint pink color is produced in the test drop by a drop of cresol red indicator solution (0.01%). Again add 10 ml. of the bromate reagent and boil for fifteen minutes.

On removing the beaker from the source of the heat, the mixed precipitate will settle quickly, leaving a mother liquor containing the platinum. Filter the solution by suction, using a porcelain filtering crucible having solid walls and a porous base.

It is highly desirable to avoid the use of filter paper when repeated precipitations are to be made. The material of which the paper is composed undoubtedly reacts with acids and probably forms small quantities of organic compounds with the platinum metals which are not easily hydrolyzed. Iridium dioxide, which dissolves much less readily than either palladium or rhodium dioxide, tends to stain paper pulp. The stain cannot always be removed by washing. These difficulties are avoided if the porcelain filtering crucible is used. Furthermore, such crucibles have the advantage that concentrated HCl can be used to dissolve the hydrated dioxides, and considerable time is saved in preparing the solution for subsequent treatment.

Pour the supernatant liquid through first, then transfer the precipitate. Rinse the beaker and wash the precipitate with a hot 1% solution of sodium chloride, the acidity of which has been adjusted to between pH 6 and 7. Place the crucible with the precipitate, and also the stirring rod, in the beaker used for the precipitation. It may be necessary to remove a small amount of the precipitate which has crept over the lip of the beaker during filtration. It is preferable to do this with moistened crystals of sodium chloride, on the finger, rather than to use paper or a rubber policeman. Replace the watch glass and add from 10 to 20 ml. of HCl, pouring most of it into the crucible. Place the covered beaker on the steam-bath. The rhodium and palladium compounds will dissolve quickly, the iridium dioxide much more slowly. Carefully lift the crucible with the stirring rod, wash it with water and place it in a 250-ml. beaker. Pour 5 ml. of HCl into the crucible. Cover the beaker with a watch glass and set it on the steam-bath. This treatment will usually leach out the small quantity of metal chlorides in the porous bottom. This operation should

be repeated with fresh acid to ensure complete removal. Combine the leachings with the main portion of the dissolved precipitate, add 2 g. of sodium chloride, and evaporate to dryness on the steam-bath. Add 2 ml. of HCl, dilute the solution to 300 ml. with water, and repeat the precipitation of the hydrated dioxides. Two such precipitations are sufficient ordinarily to effect the complete separation of platinum from palladium, rhodium and iridium.

Add 20 ml. of HCl to each of the filtrates obtained from the hydrolytic precipitation of the dioxides of palladium, rhodium and iridium. Carefully warm the solutions until they become quiescent. Partially concentrate the filtrates, combine them and then evaporate to dryness. Make certain that all of the bromate is destroyed, by evaporation with HCl. Dilute the yellow platinum solution somewhat and filter it. Wash the filter with diluted HCl (1 : 99). Dilute the filtered solution to about 400 ml. with water and have it contain 5 ml. of HCl in each 100 ml. volume.

Precipitate the platinum, in a hot solution, with hydrogen sulfide, using a rapid stream. Continue the passage of hydrogen sulfide as the solution cools somewhat, to ensure complete precipitation.

Filter the solution and wash the precipitate with diluted HCl (1 : 99). Ignite the dried filter and precipitate in a porcelain crucible. Leach the metal residue with diluted HCl, transfer it to a filter and wash it thoroughly with hot water. Ignite the filter and metal again strongly in air. Weigh the residue as metallic platinum.[4]

B. WEIGHING AS A SALT

1. The procedure is the same as under *A*. The $(NH_4)_2PtCl_6$ precipitate is washed on a weighed Gooch crucible with alcohol. The crucible and contents are dried at a temperature below 100° C. Cool in a desiccator and weigh as $(NH_4)_2PtCl_6$.

$$\text{Wt. of } (NH_4)_2PtCl_6 \text{ found} \times \frac{\text{At. wt. of Pt}}{\text{Mol. wt. of } (NH_4)_2PtCl_6} \times \frac{100}{\text{Wt. of sample}}$$
$$= \text{per cent of Pt in material.}^{5}$$

2. After proceeding as described under *A*, the platinum is precipitated with potassium chloride as K_2PtCl_6. Transfer to a weighed Gooch crucible and wash well with alcohol. Dry below 100° C., cool in a desiccator and weigh as K_2PtCl_6.

$$\text{Wt. of } K_2PtCl_6 \text{ found} \times \frac{\text{At. wt. of Pt}}{\text{Mol. wt. of } K_2PtCl_6} \times \frac{100}{\text{Wt. of sample}}$$
$$= \text{per cent of Pt in material.}^{6}$$

C. DETERMINATION OF PLATINUM BY ELECTRO-ANALYSIS

When platinum solutions are acidulated with sulfuric acid and acted upon by a feeble current they give up the metal as a bright deposit upon the elec-

[4] Gilchrist and Wichers, J. Am. Chem. Soc., 57, 2565 (1935).
[5] Factor $(NH_4)_2PtCl_6$ to Pt = 0.4397.
[6] Factor K_2PtCl_6 to Pt = 0.4016.

trode. If platinum is used as the electrode, first coat it with a layer of copper and deposit the platinum upon the copper. Wash with water and alcohol and after drying, weigh.

$$\text{Wt. of electrode} + \text{Cu} + \text{Pt} - \text{Wt. of electrode} + \text{Cu} = \text{Wt. of Pt.}$$

$$\frac{\text{Wt. of Pt}}{\text{Wt. of sample taken}} \times 100 = \text{per cent of Pt in material.}$$

Dr. E. F. Smith, in his work on " Electro-Analysis " recommends that the K_2PtCl_6 be dissolved in water and slightly acidulated with H_2SO_4 (2 or 3% by vol.) and after heating to about 60 to 65° C. and electrolyzing with $N.D._{100} = .05$ ampere and 1.2 volts, the platinum will be completely precipitated in from four to five hours in a perfectly adherent form. A rotating anode will precipitate the platinum much quicker.

PALLADIUM

Element, Palladium. **Pd.** ***at.wt.*** **106.7;** ***sp.gr.*** **11.9;** ***m.p.*** **1549°C.;** ***oxides,*** **PdO, PdO_2**

DETECTION

This metal is also found associated with platinum and iridium as well as ruthenium, rhodium, and osmium. It occurs in the metallic state sometimes with gold and silver. It resembles platinum as to luster and color. Palladium sponge when heated slightly gives a rainbow effect due to the formation of oxides. Hydrogen passed over the sponge restores it to the original color. It dissolves in HNO_3 and boiling H_2SO_4. HCl has little action upon it. It is readily soluble in aqua regia, forming $PdCl_2$. $PdCl_4$ is unstable.

Palladium monoxide, PdO, is formed by a long-continued heating of the spongy metal in a current of oxygen at a temperature from 700 to 840° C. or by heating a mixture of a palladium salt with potassium carbonate. The pure hydrated oxide is best prepared by the hydrolysis of the nitrate.

It turns diphenylamine blue; and it reduces hydrogen peroxide with difficulty.[7]

Palladium dioxide, PdO_2, is obtained in an impure hydrated form as a brown precipitate by the addition of caustic soda to potassium palladichloride. This is soluble in acids, but becomes less soluble when preserved. It can be obtained free from alkali and basic salts by the anodic oxidation of the nitrate, but it is not quite free from monoxide. The dioxide very readily decomposes into the monoxide and oxygen, and cannot be obtained in the anhydrous state. It acts as a vigorous oxidizing agent and decomposes hydrogen peroxide.

Alkalies precipitate in a concentrated solution a dark-brown precipitate soluble in an excess of the reagent. If boiled a brown palladous hydroxide is precipitated. The anhydrous oxide is black.

Ammonia added to a concentrated solution gives a flesh-red precipitate, $Pd(NH_3)_4Cl_2 \cdot PdCl_2$, soluble in excess of ammonia. If HCl is added to this solution, the yellow compound of palladosamine chloride, $Pd(NH_3Cl)_2$, is deposited.

Sulfur dioxide precipitates the metal from the nitrate or sulfate solution but not from the chloride.

Cuprous chloride precipitates the metal from the sulfate, nitrate and chloride solutions when they are not too strongly acid.

Mercuric cyanide precipitates a yellowish-white gelatinous precipitate, $Pd(CN)_2$, insoluble in dilute acids, but dissolving in ammonia and in potassium cyanide to $K_2Pd(CN)_4$.

Potassium iodide precipitates black palladous iodide, PdI_2, insoluble in water, alcohol, and ether, but soluble in an excess of reagent.

[7] A Comprehensive Treatise on Inorganic and Theoretical Chemistry, J. W. Mellor, Vol. XV, p. 656 (1936).

Hydrogen sulfide precipitates black palladous sulfide, PdS, soluble in HCl and aqua regia, but insoluble in $(NH_4)_2S$.

Ferrous sulfate slowly produces a black precipitate of metallic palladium from the nitrate.

Ammonium chloride precipitates palladium as $(NH_4)_2PdCl_4$ from the nitrate.

Formic acid, zinc and iron reduce to metallic palladium.

Soluble carbonates precipitate brown palladous hydroxide, $Pd(OH)_2$, soluble in excess, and reprecipitated on boiling.

Phosphuretted hydrogen gas precipitates palladium phosphide. *(Difference from Pt, Rh, and Ir).*

Alcohol precipitates, on boiling, metallic palladium.

Alkaline tartrates and citrates form yellow precipitates in a neutral solution from the nitrate.

Stannous chloride produces a brownish-black precipitate, soluble in hydrochloric acid to an intense green solution.

Potassium bisulfate attacks the metal readily.

An alcoholic solution of iodine dropped on the metal will turn black.

Acetylene gas passed through an acidified solution containing Pd produces a brown precipitate which, upon ignition, yields Pd. In this way Pd may be quantitatively separated from Cu.

ESTIMATION

Palladium is determined in alloys, ores, jewelers' sweeps, etc.

PREPARATION AND SOLUTION OF THE SAMPLE

The solubility of palladium has been taken up under Detection. Palladium when alloyed with platinum, or an alloy of platinum, iridium and palladium, dissolves with the other metals in aqua regia as the chloride. When palladium is alloyed with silver the palladium and silver are dissolved in HNO_3, from which the silver can be separated.

SEPARATIONS

Separation of Palladium from Platinum and Iridium.—The chlorides of palladium, platinum and iridium in solution must be free from HNO_3. The platinum and the iridium are precipitated with NH_4Cl, leaving the palladium in solution. The precipitate is put on a filter and washed free from Pd with NH_4Cl solution and alcohol.

Separation of Palladium from Silver and Gold.—At least three times the weight of the gold in silver should be present in the alloy in order to separate the silver and palladium from the gold. The silver and the palladium will dissolve in HNO_3, leaving the gold as the residue. This is filtered off and the silver may be precipitated with HCl. The silver chloride is filtered off and washed with hot water acidulated with HCl until free from palladium. Since AgCl tends to retain palladium it is advisable to redissolve the silver with HNO_3 after reduction of AgCl and reprecipitate the chloride to obtain a complete separation of palladium.

Separation of Palladium from Platinum.—The chlorides of platinum and palladium being free from HNO_3 and having an excess of HCl is diluted with water. A 10% solution of potassium iodide is added until all of the palladium is precipitated. Avoid adding a large excess. The precipitate of PdI_2 is filtered off and washed free from platinum and alkali with water slightly acidulated with HCl. The filter is ignited to metallic sponge in a current of hydrogen. See glyoxime method on page 724.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF PALLADIUM

1. The palladium is precipitated from the solution by granulated zinc, the solution having a small amount of free hydrochloric acid. The residue, after the zinc is dissolved, is put on a filter and washed free from impurities. Ignite the filter and dissolve in a small amount of aqua regia and evaporate to a syrupy consistency. Dilute with a small amount of water and add a few drops of HNO_3; precipitate the palladium with NH_4Cl crystals. Heat for a few minutes and let cool. Filter, wash with alcohol, and ignite. Reduce in hydrogen or moisten with formic acid to reduce to metal any oxide that may have formed. Dry and weigh as metallic palladium.

2. With the solution containing about one-fifth the volume of free HCl, the palladium is precipitated with 10% KI solution. Heat to nearly boiling, filter, wash free from iron, etc., with 1 : 4 HCl. Ignite, cool, reduce in hydrogen or moisten with formic acid, dry and weigh as metallic Pd.

3. The filtrate from the platinum precipitation or the nearly neutral solution containing the Pd is made to about 150 ml., and the Pd is precipitated by

adding a solution of dimethylglyoxime (1% solution in alcohol). Bring to boiling and let stand overnight if convenient. Filter on a weighed Gooch crucible and wash with hot water slightly acidified with HCl, then with alcohol. Dry and weigh as $(C_8H_{14}N_4O_4)Pd$, which contains 31.67% Pd.

4. The nitric acid in the palladium solution is expelled by evaporating with HCl. Neutralize the chloride solution almost completely with sodium carbonate and mix the solution with a solution of mercuric cyanide, $Hg(CN)_2$, and heat gently for some time. Let stand until cool, overnight if convenient. A yellowish-white precipitate of $Pd(CN)_2$ is formed. Filter, wash with 1% $Hg(CN)_2$ solution, ignite and reduce in hydrogen to metal, or reduce with formic acid, dry, and weigh as metallic Pd.

5. The filtrate from the platinum precipitation is made neutral or slightly alkaline with Na_2CO_3 solution and an excess of formic acid is added. Boil until all the palladium is precipitated or the solution becomes clear. Filter, wash with hot water, ignite, reduce in hydrogen or with formic acid and weigh as metallic Pd.

6. The hydrated dioxides of palladium, rhodium and iridium, after separating the platinum (see A4 under platinum), are dissolved in HCl. Filter the solution and dilute it to a volume of about 400 ml. Add a sufficient volume of a 1% solution of dimethylglyoxime in 95% ethyl alcohol to precipitate all of the palladium (2.2 g. of the solid reagent is required for 1 g. of palladium). An excess of the reagent amounting to 10% should be added to ensure complete precipitation. Let the solution stand for one hour and then filter it. The manner of filtration will depend upon the form in which the palladium is to be determined. Wash the precipitate with dilute HCl (1 : 99), and finally with hot water. The precipitate can be washed with a considerable volume of water without a trace of it dissolving. A single precipitation of the palladium is sufficient to separate it completely from rhodium and iridium.

Palladium dimethylglyoxime is sufficiently stable and constant in composition to be dried and weighed. If the determination is to be made in this manner, catch the precipitate in a porcelain or glass filtering crucible, using suction. Wash the precipitate as previously directed and dry it at 110° C. for one hour. Calculate the quantity of palladium, using the theoretical factor, 0.3167.

If the palladium is to be determined as metal, catch the precipitate on an ashless filter. Wipe the inner walls of the beaker and also the glass rod with a small piece of ashless paper. Wrap the filter and precipitate in a second filter and place them in a porcelain crucible. Dry them, and ignite them carefully in the air. Only sufficient heat should be supplied to keep the papers smoking gently. Ignite the charred residue strongly in air, and then in hydrogen. Ignite the metallic palladium in CO_2 for two minutes and cool it in CO_2. Weigh the residue as metallic palladium.[8]

[8] Gilchrist and Wichers, J. Am. Chem. Soc., 57, 2565 (1935).

DETERMINATION OF PLATINUM AND PALLADIUM[1]

SPECIAL METHODS

Gold Bar.—Dissolve a 100-gram sample in aqua regia, and expel the nitric acid by evaporation and the addition of small amounts of hydrochloric acid. Take up with a few ml. of dilute hydrochloric acid. If there should be present a large amount of reduced gold, add a few drops of nitric acid and heat the solution for a few minutes. Dilute to 800 ml. with water, and let it stand in a cool place until solution clears. Filter off silver chloride and wash it with cold water. Pass sulfur dioxide gas through the filtrate to reduce the gold (palladium, etc., is also reduced). Decant the clear solution on a tight filter paper, and wash several times with hot water by decantation. Then pour over the gold in the beaker, 50 ml. of nitric acid, and boil for a few minutes to dissolve the reduced palladium. Add 50 ml. of hot water and filter on the same filter paper and wash several times with hot water. Add 15 ml. of sulfuric acid to the filtrate, evaporate and heat to heavy fumes. Cool, dilute to 200 ml. with water and boil for a few minutes, and filter off any gold and lead sulfate if present. Now pass hydrogen sulfide gas through the hot solution to precipitate the sulfides of platinum and palladium, etc. Filter and wash with hot water. Place the filter paper with the precipitate in a porcelain crucible, dry, burn and ignite. Now touch the residue with the reducing flame of a Bunsen burner to reduce to metal any oxide of palladium that may have formed. Dissolve the residue with a few ml. of aqua regia, and transfer the solution to a tall 300-ml. beaker, and evaporate carefully to dryness on a steam or sand bath. Then moisten the residue with hydrochloric acid and evaporate to dryness again. Moisten the dry residue once more with hydrochloric acid and evaporate to dryness.

Now take up with 16 ml. of hydrochloric acid and 4 ml. of water, cover beaker and boil gently for a moment. Filter on a small filter paper and wash with a small stream of hot water. Discard the residue. Dilute filtrate to 60-ml., cover beaker and heat to near boiling point. Then add 16 grams of ammonium chloride and heat gently to near boiling until all ammonium chloride is in solution. Remove beaker from the hot plate, and let it stand over night in a cool place. Filter rapidly (using suction) on a tight, double filter paper, and wash with ammonium chloride solution (200 grams per liter of water). As the ammonium chloroplatinate is somewhat soluble if exposed to air, the precipitate should be covered with the wash solution all the time during filtration. Then before the ammonium chloride solution is all sucked through, wash once or twice with 95% grain alcohol. Save filtrate for palladium determination. Place the filter paper with the precipitate in a porcelain crucible, so that the precipitate does not come in contact with the sides of the crucible; if it does, a platinum mirror will form, which cannot be removed. Dry gently and smoke off the filter paper (without burning it with a flame), and finally ignite at a bright red heat. Cool and weigh metallic platinum.

Add to the filtrate from the ammonium chloroplatinate precipitate, 16 ml. of nitric acid, stir, cover beaker, placing a glass triangle under the watch glass,

[1] Contributed by F. Jaeger, Chemist, Nichols Copper Co.

and let it stand over night on steam plate. When the solution is supersaturated, as indicated when half of the solution is filled with ammonia salts, remove the beaker from the steam plate and cool the solution. Filter off the ammonium chloropalladate just like the platinum salt and wash with ammonium nitrate solution (200 grams per liter of water). Finally wash with 95% grain alcohol. The solubility of ammonium chloropalladate is greater than of the platinum salt when exposed to air, therefore great care must be taken in filtering it. Place the precipitate with the filter paper in a porcelain crucible, dry, smoke off filter paper and finally ignite at a bright red heat. When cool, reduce any oxide that may have formed with the reducing flame of a Bunsen burner. Cool and weigh metallic palladium.

To confirm that all platinum and palladium is precipitated, neutralize the filtrate from the ammonium chloropalladate with a saturated solution of sodium carbonate, then add 30 ml. of formic acid, and boil for about one hour. Any platinum or palladium if still present will be precipitated as black powder.

NOTE.—All evaporations should be made on a steam or sand bath, if not, incomplete precipitation of platinum will be obtained.

Refined Silver.—Weigh out 1,000-gram sample and dissolve it with dilute nitric acid. Filter off the gold and any undissolved platinum, and then separate the gold from the platinum as described under "Gold Bar," and add the solution to the main filtrate. Dilute the filtrate from the gold residue, so that there will be 10 grams of silver per liter of solution, and then add a slight excess of hydrochloric acid to precipitate all the silver. Stir well and let it settle. Decant the clear solution and wash the precipitate on a Buechner funnel with cold water. Evaporate the filtrate to a small volume. Now mix the silver chloride, with about ten times its weight, with soda ash (which contains a small amount of corn starch) and dry. Place the mass in 30-gram crucibles, and fuse for about 30 minutes. Pour in molds. When cool, hammer off excess of slag, and finally boil with hydrochloric acid to clean the silver buttons. Then dissolve with dilute nitric acid and precipitate silver as silver chloride as already described. Another silver chloride precipitation will be necessary to separate all platinum and palladium from the silver.

Combine all filtrates and evaporate to dryness on steam plate. Take up with a few ml. of hydrochloric acid and water, filter off the silver chloride and wash with cold water. This small amount of silver chloride carries down considerable platinum and palladium. Therefore place the filter paper with the silver chloride in a 3-inch scorifier, dry, add 40 grams of test lead and a pinch of borax and scorify. Then cupel the lead button. Dissolve the silver buttons with dilute nitric acid and reprecipitate silver with hydrochloric acid. Finally when the pure white color of the silver chloride indicates that it is free from platinum and palladium, evaporate the filtrate to dryness on steam plate. Take up with 16 ml. of hydrochloric acid and 4 ml. of water. Boil for a minute, filter, and precipitate platinum and palladium as described under "Gold Bar."

Copper Anode Slimes.—Take a 1,000-gram sample. Weigh out 3 gram portions into 3-inch scorifiers and mix each with 40 grams of test lead and a

pinch of borax and litharge. Scorify and cupel. Dissolve silver buttons with dilute nitric acid, and proceed as described under "Refined Silver."

DETERMINATION OF PLATINUM AND PALLADIUM IN REFINED GOLD [10]

The sample may be in the shape of drillings, but from a bar it is easier to roll the gold into a thin ribbon.

Fifty grams [11] of gold sample is sufficient for gold which has been parted with sulfuric and nitric acids.

Dissolve sample in a 1,500-ml. beaker with 50 ml. of nitric acid (1.42) and 150 ml. of hydrochloric acid (1.19) using no water. Heating is not necessary. After complete solution of the sample, evaporate solution to a syrup of about 40 ml. volume, taking care not to evaporate too far, otherwise, some gold will become reduced and separate out; add 100 ml. of hydrochloric acid and re-evaporate the solution to syrup, repeating this operation four times in order to remove all nitric acid.

After the last evaporation, dilute with hot water, boil, add about 50 ml. hydrochloric acid (1.19) to clear up solution. The volume of solution should be about 500 ml.

To the boiling solution [12] gradually add a mixture of 50 grams ammonium oxalate and 50 grams oxalic acid, which should precipitate all the gold, but should there be any doubt add more of the mixture of the salts. Dilute the solution to about 1,000 ml. in volume and allow to settle in a warm place over night.

Filter off the gold, washing by decantation into a 1,500-ml. beaker. For extreme accuracy, this gold may be redissolved, re-evaporated and reprecipitated, this time with sulfur dioxide gas. This is more of a precautionary measure, for as a rule, no platinum or palladium will be found with the gold.

[10] Contributed by S. Skowronski, Chemist, Raritan Copper Works, Perth Amboy, N. J.

[11] For gold which has been electrolytically refined by the Wohlwill process, 100 grams of gold should be taken as a sample, doubling the quantity of acid necessary for the solution.

[12] Sulfur dioxide gas is not recommended for the precipitation of gold as gold bullions contain a trace of tellurium, and in the presence of tellurium, palladium is precipitated as a telluride by sulfur dioxide gas. The gold precipitated with oxalic acid is free from palladium telluride and therefore may be reprecipitated with sulfur dioxide gas if a reprecipitation is thought necessary.

To the solution from the gold add 5 grams of 30 mesh C.P. zinc. This precipitates any gold left in the solution along with the silver, platinum, palladium, tellurium, copper, etc.

Filter as soon as precipitation is complete and wash by decantation keeping as much of the precipitate in the beaker as possible. Ignite filter paper and transfer residue and precipitate to a 250-ml. beaker, dissolve in 10 ml. aqua regia and after complete solution, add 5 ml. sulfuric acid (1.84), evaporate to fumes of SO_3 and fume well,[13] cool, dilute to 100 ml. bring solution to boiling and add 1 drop of hydrochloric acid to precipitate the silver, filter in a 400-ml. beaker, dilute filtrate to 200 ml. volume, add 5 ml. hydrochloric acid (1.19), and precipitate palladium with .5 gram of dimethylglyoxime dissolved in 50 ml. of boiling water.[14]

Palladium dimethylglyoxime, canary yellow in color, which possesses the same physical characteristics as the corresponding nickel salt, at once separates out. Allow to settle in a warm place for about five minutes. Filter in a Gooch crucible, wash with hot water, dry at 110° C. and weigh. Factor .3168.

To the filtrate from the palladium add 2 grams of 30-mesh C.P. zinc, which precipitates the platinum. Filter, ignite precipitate and dissolve in aqua regia. Remove nitric acid by three evaporations with hydrochloric acid (1.19), taking care not to evaporate solution to dryness.[15] After the last evaporation, take up with not more than 10 ml. of water and a few drops of hydrochloric acid. If necessary, filter, keeping volume of 10 ml., add 2 grams of ammonium chloride, stir well, add 10 ml. of alcohol, and let stand one hour with an occasional stirring.

Filter off ammonium chloroplatinate in small Gooch crucible and ignite to platinum in the usual manner.

Separation of Platinum and Gold.—In place of the procedures given on page 715 it is often preferable to precipitate gold first by means of sulfur dioxide, then reprecipitating with oxalic acid from weakly acid solution to obtain gold free from platinum.

Separation of Platinum and Ruthenium.—According to Deville and his co-workers the ammonium chloride separation is unsatisfactory owing to contamination of the ammonium chloroplatinate with ruthenium. The ruthenium may be separated by volatilization with chlorine passed into the alkaline solution of platinum and ruthenium. See page 738.

[13] The platinum and palladium after solution in aqua regia, and addition of sulfuric acid, should be well fumed, in order to reduce any gold remaining in the solution to the metallic condition. It is very essential that all the gold is removed at this stage, otherwise it is liable to contaminate the palladium dimethylglyoxime.

[14] Palladium is best precipitated with dimethylglyoxime in a 3–5% acid solution, gold if present will be reduced to the metallic condition and should be removed before hand. Alcohol is not recommended as the solvent for the dimethylglyoxime, as it slows up the precipitation of the palladium. A hot water solution works quicker, and should be filtered to remove insoluble matter before addition to the palladium solution.

The precipitation should be carried out in a cold solution, since platinum will contaminate the palladium precipitate if the dimethylglyoxime reagent is added to a hot solution.

[15] Any solutions containing platinum should never be evaporated to dryness, as platinum is easily reduced in baking to the "platinous" condition which is not precipitated with ammonium chloride.

QUANTITATIVE SEPARATION OF THE ELEMENTS OF THE PLATINUM GROUP[1]

Dissolve the material in aqua regia and filter off the insol. Ignite the residue and fuse in a nickel crucible with Na_2O_2. Cool, place in a beaker containing a little water and acidify with HCl. Combine the solutions, place in a distillation flask, make alkaline with NaOH and distil with a current of chlorine gas, catching the distillate in NaOH.

<table>
<tr>
<td rowspan="5">Distillate: Ru, Os. Acidify with HCl and pass in H_2S. Filter off sulfides and ignite in a boat in a combustion tube in a current of oxygen, catching the volatile OsO_4 in a solution of NaOH and alcohol. Determine Os in this solution, and weigh RuO_2 remaining in the boat.</td>
<td colspan="6">The remaining solution is boiled to expel chlorine and then concentrated NH_4Cl solution is added and sufficient 95% alcohol to double the volume of the solution.</td>
</tr>
<tr>
<td colspan="3">Precipitate: Pt, Ir, some Rh, traces of Pd. Ignite in an atmosphere of hydrogen, extract residue with dilute aqua regia (1 part acids to 4 parts water).</td>
<td colspan="3">Filtrate: Rh, Pd, some Pt, Ir, and any Fe, Ni, Cu that was present in sample. Nearly neutralize with NH_4OH and pass in H_2S gas.</td>
</tr>
<tr>
<td colspan="2">Residue: Ir, Rh. Fuse with $KHSO_4$, extract with water and dilute H_2SO_4. Repeat fusion and extraction. Combine filtrates, washing residue.</td>
<td>Solution: Pt with traces of Pd, Ir, Rh.</td>
<td colspan="2">Precipitate: sulfides of Pd, Rh, Au, Cu. Ignite and digest with HCl, filter and repeat ignition and extraction of residue. Combine extracts.</td>
<td rowspan="2">Filtrate: Ni, Fe, some Au and Rh. Evaporate to dryness with HNO_3 and ignite. Extract Fe and Ni with HCl. Ignite residue (B) and combine with (A) and (C).</td>
</tr>
<tr>
<td>Residue: Ir, trace Rh.</td>
<td colspan="2">Solution: (A) Rh. Boil with Na_2CO_3, then acidify with HCl and filter. Ignite residue and combine with Rh from (B) and (C).</td>
<td>Residue (C): Rh. Combine with (A) and (B).</td>
<td>Filtrate: Pd, Cu. Add KCl and alcohol. If Pd is present, it will precipitate as K_2PdCl_4.</td>
</tr>
<tr>
<td colspan="6">Combine residues (A), (B) and (C) containing Au and Rh. Dissolve out Au by extraction with aqua regia. Rh is left as a residue.</td>
</tr>
</table>

[1] Mellor, A Treatise on Quantitative Inorganic Analysis (Griffin and Co., 1913).

RARER ELEMENTS OF THE ALLIED PLATINUM METALS [16]

IRIDIUM

Element, Iridium. **Ir.** *at.wt.* **193.1;** *sp.gr.* **22.4;** *m.p.* **2350° C.?** *oxides,* **IrO_2, Ir_2O_3**

DETECTION

Iridium is found associated with platinum. The element is insoluble in all acids, including aqua regia. Chlorine is the best reagent which forms the chlorides of iridium and yields compounds with other chlorides as K_2IrCl_6. If the element is heated in a stream of chlorine in the presence of potassium chloride there forms a salt, K_2IrCl_6, which is sparingly soluble and is used in the separation of iridium.

The oxide, Ir_2O_3, is formed when K_2IrCl_6 is mixed with sodium carbonate and gently fused at a dull red heat.

$$2K_2IrCl_6+4Na_2CO_3=Ir_2O_3+8NaCl+4KCl+4CO_2+O.$$

The fusion is dissolved in water containing ammonium chloride. Filter the residue and after igniting to expel the ammonium chloride, treat with dilute acid in order to remove the small quantity of alkali. A bluish-black powder is thus obtained which begins to decompose when heated above 800 degrees, and at temperatures somewhat above 1000 degrees is completely broken up into oxygen and the metal.[17]

The dioxide, IrO_2, is a black powder obtained by heating the hydroxide in a current of carbon dioxide. It is insoluble in acids.[17]

Caustic Alkalies produce in a boiling solution a dark-blue precipitate of $Ir(OH)_4$ insoluble in all acids except HCl.

Potassium chloride forms the double salt of K_2IrCl_6, which is black and is difficultly soluble in water.

Ammonium chloride precipitates black $(NH_4)_2IrCl_6$, which is difficultly soluble in water.

Hydrogen sulfide precipitates black Ir_2S_3, soluble in $(NH_4)_2S$.

Metallic zinc precipitates from an acid solution black metallic iridium.

Formic acid and sulfurous acid precipitate black metallic iridium from hot solutions.

Lead acetate gives a gray-brown precipitate.

[16] Chapter contributed by R. E. Hickman.
[17] "Treatise on Chemistry," Roscoe and Schorlemmer.

ESTIMATION

Substances in which iridium is determined are: platinum scrap, jewelers' sweeps, contact points, ores. Iridium is weighed as the metal.

PREPARATION AND SOLUTION OF THE SAMPLE

Platinum scrap and contact points, etc., containing iridium dissolve with difficulty in aqua regia, depending on the amount of iridium present. The alloy is dissolved more quickly if it is rolled or hammered to a very thin sheet or ribbon. The alloy of platinum and iridium with an iridium content up to 10% dissolves in aqua regia slowly; an alloy of iridium content of 15% dissolves in aqua regia very slowly and the aqua regia will likely have to be replenished from time to time. An alloy of 25% iridium is practically insoluble in aqua regia. The filings from sweeps, etc., can be dissolved by aqua regia the same as the scrap. After expelling the HNO_3 the platinum and the iridium are precipitated together with NH_4Cl as $(NH_4)_2PtCl_6$ and $(NH_4)_2IrCl_6$. The iridium imparts a pinkish to a scarlet color to the salt.

If the iridium content is too high to be dissolved in aqua regia the metal can be mixed with NaCl, heated to a dull red heat in a porcelain or silica tube, and moist chlorine passed over the mixture. The iridium will be in the form of a double chloride which dissolves in water. After filtering the solution and evaporating with HCl, the iridium as well as the platinum is precipitated with NH_4Cl or H_2S. This is a convenient way on a larger scale to dissolve osmiridium in ores. The writer has had good results with this operation.

When the iridium is contaminated with a large amount of impurities, it may be reduced from the solution with zinc, and the impurities dissolved by HNO_3 and dilute aqua regia; the residue is washed and dried as iridium.

Clean osmiridium grains are also brought into solution by sintering with BaO_2 and $Ba(NO_3)_2$ and dissolving in water acidulated with HCl. A fusion can be made with KNO_3, $NaNO_3$, or Na_2O_2 and NaOH or KOH yielding a soluble ruthenate and osmate, and leaving the iridium and rhodium as insoluble oxides.

SEPARATIONS

Separation of Iridium from Platinum.—See Separation of Pt from Ir.

If the platinum and iridium are alloyed with at least ten times their weight of silver or lead and the alloy dissolved in HNO_3, the silver or lead and the platinum dissolve, leaving the iridium insoluble. After washing the residue,

treat with a small amount of dilute aqua regia to dissolve any platinum that may be present. If the alloy contains more than a few milligrams of platinum, it will be necessary to add fine gold when cupelling to prevent the platinum from becoming colloidal.

If the alloy is made with silver only, hot concentrated H_2SO_4 can be used in place of HNO_3 to dissolve the silver. The iridium and platinum which are insoluble are treated with dilute aqua regia to remove the platinum leaving a residue of iridium and a small amount of silver chloride.

Separation from Osmium.—Osmium is removed by distillation. See Os. For other separations see under Rh and Ru.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF IRIDIUM

1. BY REDUCTION WITH ZINC

The solution of iridium and platinum is treated with C.P. granulated zinc and 5% free HCl. The iridium and the platinum are precipitated as fine black metal. The black metal is washed free from impurities and the platinum is dissolved in dilute aqua regia as described under the Separations. The insoluble portion is dried, ignited, reduced with hydrogen and weighed as metallic iridium.[18]

2. BY IGNITING THE SALT $(NH_4)_2IrCl_6$

The percentage of iridium in the salt may be judged fairly well by the color, by comparing with standard iridio-platinum salts. The salt is filtered, washed with alcohol and carefully ignited and weighed as iridio-platinum sponge metal. The percentage of iridium in the sample can be calculated from the weight of the iridium obtained. The two metals are treated as stated under 3 below.

3. BY OBTAINING IT AS A RESIDUE

The iridium and the platinum, etc., are alloyed with at least ten times their weight of silver and the alloy dissolved in HNO_3. The residue will be a small amount of platinum, gold if any present, and iridium. Add a small amount of dilute aqua regia, which will dissolve the gold and the rest of the platinum, leaving the iridium as a black residue. This is filtered and washed alternately

[18] When the Pt metals are precipitated with Zn, Mg, Al, etc., the precipitate will invariably contain some of the metal used as reagent. It is very difficult to make a complete precipitation of Ir.

with hot water and hot dilute NH_4OH until free from silver chloride. Ignite, reduce in hydrogen, cool in CO_2 and weigh as metallic iridium. Hot concentrated H_2SO_4 can be used in place of HNO_3 as described under Separations on page 731.

One part of the iridium material is alloyed with ten parts of lead. This is packed in a graphite capsule, and the whole embedded in charcoal in an ordinary assay crucible. Heat to a high temperature in a furnace for several hours. When the crucible and contents are cold, remove the lead and clean well. Treat the lead with dilute HNO_3, thus removing the lead and leaving the iridium as the residue. Wash thoroughly and treat the residue with dilute aqua regia, which leaves the residue as pure iridium.[19] If other metals of the platinum group are present, see separations under those metals.

The residue containing iridium, rhodium, ruthenium and osmium is fused with 5 grams KOH and one gram KNO_3, and the ruthenium as well as the osmium are distilled with chlorine as explained under ruthenium. The solution in the distilling flask is acidified with HCl and zinced completely, or boiled with alcohol for about half an hour after making alkaline with KOH. The precipitate is filtered, washed thoroughly and ignited. This residue of impure iridium and rhodium is scorified with test lead, the lead button is cleaned very thoroughly and dissolved in dilute HNO_3. The residue is then treated with H_2SO_4 as explained under Separation of Rh from Ir.

After filtering the rhodium sulfate, the iridium residue is washed well with a hot 10% solution of ammonium acetate until free from lead sulfate. Ignite and boil with dilute HNO_3 to dissolve any silver that may be present. Filter, wash with hot water and dilute NH_4OH, ignite and treat with hydrofluoric acid in a platinum dish to remove silica. Take up with hot water, filter, wash well, ignite, reduce in hydrogen, cool in CO_2 and weigh as metallic iridium.

It is extremely difficult to separate the almost inappreciable traces of ruthenium and rhodium from iridium. The spectroscopic detection of impurities in iridium is not so convenient as is the case with some other platinum metals because the spectrum of iridium is complex and many of the sensitive lines of the other platinum metals are coincident with iridium lines unless great dispersion is used. (A Comprehensive Treatise on Inorganic and Theoretical Chemistry, J. W. Mellor, Vol. XV, p. 734, 1936).

4. DETERMINATION OF IRIDIUM

Method of Deville and Stas, Modified by Gilchrist[20]

1. **Lead Fusion.**—Fuse the carefully sampled platinum alloy with 10 times its weight of granular test lead for a period of one hour at a temperature of about 1000° C. A covered crucible, whose outside dimensions are 4 cm. in diameter and 7 cm. in height, machined from Acheson graphite, is suitable for fusions made with 20 to 40 grams of lead. The inside of the crucible should possess a slight taper to facilitate the removal of the cooled ingot. Do not pour the fusion from the crucible, but allow it to solidify, since the iridium has

[19] Very often this Ir contains lead in amounts varying from a trace to 10%.
[20] R. Gilchrist, J. Am. Chem. Soc., 45, 2820, 1923.

largely settled to the bottom of the crucible. The crucible is best heated in an electric furnace.

2. **Disintegration with Nitric Acid.**—Brush the cooled lead ingot free from carbon with a camel's hair brush and place it in a beaker. Add dilute nitric acid (one volume of nitric acid (sp.gr. 1.42) to 4 volumes of water), using 1 ml. of acid per g. of lead. Place the beaker on the steam-bath or on a hot-plate, which maintains the temperature of the solution at about 85° C. Disintegration of the lead ingot is usually complete in about two hours and leaves a rather voluminous, grayish-black mass. Dilute the solution to twice its volume and decant the liquid through a double filter, consisting of a 9-cm. paper of fine texture, on which is superimposed a 7-cm. paper of looser texture. Wash the residue quite thoroughly with hot water and pass the washings through the filters. The residue is not transferred to the filters at this point. The lead nitrate solutions and washings are best caught in an Erlenmeyer flask to make easier the detection of the presence of any residue which has passed through the filters. This is done by whirling the liquid in the flask. Return the filters to the beaker without ignition.

3. **Solution of the Lead-Platinum Alloy with Aqua Regia.**—Add in order —15 ml. of water, 5 ml. of hydrochloric acid (sp.gr. 1.18) and 0.8 ml. of nitric acid (sp.gr. 1.42) for each gram of the platinum-alloy sample taken. Heat the solution in the beaker on the steam-bath or on a hot-plate which maintains the temperature at about 85° C. The lead-platinum alloy is usually completely dissolved within one and a half hours. Dilute the solution with twice its volume of water and filter through a double filter similar to the one used for the lead nitrate solution; the iridium, insoluble in aqua regia, is in the form of fine crystals, possessing a bright metallic luster and having a high density. Pass the clear solution through the filter first and then transfer the thoroughly macerated paper. It is very important to examine the beaker to see that no iridium remains. To do this the interior of the beaker is wiped with a piece of filter paper to collect any metal adhering to the sides. Then by whirling a small quantity of water in the beaker any iridium remaining gravitates towards one place whence it can be removed with a piece of paper. Wash the filters and iridium thoroughly, first with hot water, then with hot dilute hydrochloric acid (1 : 100), and lastly with hot water. The chlorplatinic acid filtrate and washings should be examined for iridium, which may have passed through the filters, in the manner described under the nitric acid treatment. The last washings should be tested for the absence of lead.

4. **Ignition and Reduction of the Iridium.**—Place the washed filters and iridium in a porcelain crucible and dry, before igniting in air. After the destruction of the filter paper, ignite the iridium strongly with the full heat of a Tirrill burner. After all the carbon is burned out, cover the crucible with a Rose lid, preferably of quartz. Introduce in the crucible a stream of hydrogen, burning from the tip of a Rose delivery tube (a quartz tube preferred). After five minutes remove the burner and a few minutes later extinguish the hydrogen flame by momentarily breaking the current of hydrogen. This is best done by having a section of the rubber delivery tube replaced by a glass tube, one end of which can easily be disconnected. Allow the iridium to cool in an atmosphere of hydrogen and then weigh as metallic iridium.

NOTES.—In commercial analysis no effort is made to correct the weight of iridium for small amounts of ruthenium. Correction, if desired, can be made according to the original directions of Deville and Stas. ("Procés-verbaux, Comité International des Poids et Mesures," pp. 162, 191, 1877.) The correction for iron can be made by the procedure suggested by W. H. Swanger, U. S. Bureau of Standards. The iridium is fused with zinc, the excess zinc removed with hydrochloric acid, and the zinc-iridium alloy fused with potassium pyrosulfate. The fusion is digested with dilute sulfuric acid, which leaves a residue of iridium free from iron but contaminated with silica. Silica is now removed by the usual manner and pure iridium remains. This purification is necessary if iron is present in the sample since this separates with iridium. Palladium, rhodium and gold have no effect in the determination. Ruthenium separates quantitatively with the iridium. The loss of weight of iridium during the ignition periods is insignificant.

5. DETERMINATION OF IRIDIUM BY PRECIPITATION AS THE HYDRATED DIOXIDE

Iridium may be determined in either of two ways. If the solution containing both rhodium and iridium can be divided conveniently into aliquot parts, the determination of iridium is greatly simplified and the precipitations of titanium by cupferron avoided. (See 8 under Gravimetric Methods for Rhodium). The rhodium and iridium in one portion of the solution can be recovered by hydrolytic precipitation as described in the procedure for the separation of platinum. If this is done, the mixed precipitate of rhodium and iridium dioxides is washed with a hot 1% solution of ammonium chloride, neutral to brom thymol blue (pH 7), instead of with a solution of sodium chloride. The dried filter and precipitate are impregnated with a few drops of a saturated solution of ammonium chloride, in order to prevent deflagration, and carefully ignited to a mixture of the anhydrous oxides. The oxidized residue is ignited and cooled in hydrogen, and weighed as a mixture of metallic rhodium and metallic iridium. In order to calculate the quantity of iridium, it is necessary, in addition, to determine rhodium in a separate portion of the solution. (See 8 under Gravimetric Methods for Rhodium).

If the iridium cannot be determined in this way, it is necessary to recover it from the filtrates resulting from the precipitation of rhodium by titanous chloride.

Dilute the combined filtrates from the precipitation of rhodium by titanous chloride to 800 ml. Cool the solution by placing the beaker in crushed ice. Add a chilled, filtered, freshly prepared 6% solution of cupferron (ammonium salt of nitrosophenylhydroxylamine, $C_6H_5N \cdot NO \cdot ONH_4$) in slight excess. Filter the solution and wash the titanium precipitate with chilled diluted H_2SO_4 (2.5 : 97.5) containing some cupferron. The cupferron precipitate is usually slightly contaminated by iridium, but the amount does not exceed 1 mg. when about 0.2 g. of iridium is being handled. Return the filter and precipitate to the beaker, add 20 ml. of HNO_3, and heat until the precipitate is mostly decomposed. Add 20 ml. of H_2SO_4 and heat the solution until vapors of H_2SO_4 appear. Destroy the remaining organic matter by adding HNO_3, and heating. Dilute the resulting solution to 800 ml. and repeat the precipitation of the titanium. Unite the filtrates from the cupferron precipitations and evaporate until approximately 10 ml. of H_2SO_4 remains. Ensure the destruction of all organic matter. Dilute the solution somewhat and filter it.

Dilute the solution to 200 ml. with water and neutralize most of the acid contained in it with a filtered solution of sodium bicarbonate. Heat the solution to boiling and complete its neutralization with bicarbonate to the end-point of brom cresol purple, as described in the procedure for the separation of platinum. (See A4 under Platinum). Add 20 ml. of a filtered 10% solution of sodium bromate, and boil the solution for twenty to twenty-five minutes. Be sure that sufficient bromate is present to oxidize all of the iridium to the quadrivalent state. Filter the solution and wash the precipitate thoroughly with a hot 1% solution of ammonium chloride.

Place the filter and precipitate in a porcelain crucible. Dry them somewhat and then moisten them with a few drops of a saturated solution of ammonium chloride. Ignite the filter and precipitate carefully in the air and then in hydrogen. Leach the metallic residue with diluted HCl, then transfer it to a filter, and wash it with hot water. Ignite the filter and metallic residue in air. Finally, ignite the resulting oxidized metal in hydrogen, cool it in hydrogen and weigh it as metallic iridium.[21]

[21] Gilchrist and Wichers, J. Am. Chem. Soc., 57, 2565 (1935).

RUTHENIUM

Element, Ruthenium. **Ru.** ***at.wt.*** **101.7;** ***sp.gr.*** **12;** ***m.p.*** **2450° C.?** ***oxides,*** **Ru_2O_3, RuO_2, RuO_4**

DETECTION

This element is found in platinum ores, and as laurite, Ru_2S_3. It is barely soluble in aqua regia and insoluble in acid potassium sulfate. It dissolves when fused with KOH and KNO_3. The solution of the fusion when dissolved in water forms potassium ruthenate, K_2RuO_4, from which HNO_3 precipitates the hydroxide, which is soluble in HCl. The treatment with chlorine and KCl at a high temperature yields a salt of K_2RuCl_6. The salts that are most common are K_2RuCl_5 and K_2RuCl_6.

The oxide, Ru_2O_3, is formed when finely divided ruthenium is heated in the air, forming a blue powder which is insoluble in acids. It can also be obtained by heating the trihydroxide, $Ru(OH)_3$, in dry carbon dioxide which forms a black, scaly mass.[22]

Ruthenium dioxide, RuO_2, is obtained by roasting the disulfide or sulfate in contact with air. It is likewise formed when the metal is fused in an oxidizing atmosphere, when it burns with a sparkling smoky flame, and evolves an ozone-like smell.[22]

Ruthenium tetroxide, RuO_4, is formed in small quantities when the metal is heated at 1000° C. in a current of oxygen, although when heated alone it decomposes at about 106° C. It is prepared by passing chlorine into a solution of potassium nitrosochlororuthenate, or of potassium ruthenate or sodium ruthenate prepared by fusing the metal with sodium peroxide; the liquid becomes heated and the tetroxide distills over and is deposited in the receiver. The moist oxide quickly decomposes. In the dry state it is fairly stable, but decomposes in sunlight with the formation of lower oxides. It dissolves slowly in water, and the solution when it contains free chlorine or HCl may be kept without alteration for some days if light be excluded, but when pure slowly deposits a black precipitate.[22]

In addition to the above oxides, salts corresponding to the acidic oxides RuO_3 and Ru_2O_7 have been prepared.

Potassium hydroxide precipitates a black hydroxide easily soluble in HCl.

Hydrogen sulfide slowly produces brown Ru_2S_3.

Ammonium sulfide precipitates brownish black sulfide.

Metallic zinc precipitates metallic ruthenium, the solution first turning blue.

Potassium sulfocyanate gives on heating a dark brown solution.

Silver nitrate gives a rose red precipitate.

Mercurous nitrate produces a bright blue precipitate.

Zinc chloride produces a bright yellow precipitate which darkens on standing.

Potassium iodide after a time by heating precipitates the black sesqui-iodide.

[22] "Treatise on Chemistry," Roscoe and Schorlemmer. The Macmillan Co.

P-nitrosophenol yields a deep violet coloration on warming with a solution of ruthenium trichloride.[23]

Sodium thiosulfate according to C. Lea, is mixed with ammonia, and a few drops of solution of ruthenium chloride are added, and the whole boiled. A reddish-purple liquid is produced, which, unless the solutions are very dilute, is black by transmitted light. The coloration is permanent, and the liquid may be exposed to the air without alteration. This reaction is far superior to any known test for ruthenium.[24]

ESTIMATION

Ruthenium is generally estimated in alloys and ores or residues.

PREPARATION AND SOLUTION OF THE SAMPLE

When ruthenium is alloyed with platinum or gold, aqua regia dissolves these metals, forming the chlorides of platinum, gold and ruthenium. The ruthenium in ores is in the form of an alloy with platinum or osmiridium. This is fused with KNO_3 and KOH in a silver crucible, the osmium and the ruthenium forming salts as described above, while the iridium remains as an oxide.

SEPARATIONS

Separation of Ruthenium from Platinum.—The two metals are precipitated with KCl and the potassium rutheniochloride is dissolved out with cold water containing a very small amount of KCl and alcohol. The ruthenium is then precipitated from an acid solution by additions of granulated zinc.

[23] S. C. Ogburn, Jr., J. Am. Chem. Soc., 48, 2493, 2507 (1926).
[24] "Select Methods in Chemical Analysis," Sir Wm. Crookes. Longmans, Green & Co.

A separation may be made by alloying with silver and dissolving the platinum and silver in HNO_3, the ruthenium remaining as the residue. Gold should be added to the alloy to prevent the platinum from becoming colloidal. Treat with dilute aqua regia to remove the gold and a small amount of platinum. The residue will be ruthenium with a small amount of silver chloride.

From a concentrated solution of these metals precipitate the platinum with NH_4Cl. Evaporate the filtrate with potassium nitrate to dryness and boil the residue with alcohol when the residual platinum will remain behind while the ruthenium goes into solution.

Separation of Ruthenium from Iridium.—The two metals are fused with KOH and KNO_3 as described above, the ruthenium forming a salt soluble in water and the iridium remaining as an oxide.

To the solution of the two metals, sodium nitrite is added in excess, with sufficient sodium carbonate to keep the liquid neutral or alkaline. The whole is boiled until an orange color appears. The ruthenium and the iridium are converted into soluble double nitrites. Sodium sulfide is then added, small quantities at a time until the precipitated ruthenium sulfide is dissolved in the excess of alkaline sulfide. At first the addition of the sulfide gives the characteristic crimson tint due to ruthenium, but this quickly disappears and gives a bright chocolate-colored precipitate. The solution is boiled for a few minutes, and allowed to become perfectly cold and then dilute HCl cautiously added until the dissolved ruthenium sulfide is precipitated and the solution is faintly acid. The solution is filtered and the precipitate washed with hot water. The filtrate will be free from ruthenium.[25]

The fusion with KOH and KNO_3 as described above is dissolved in water in a flask or retort; chlorine is passed through this solution and thence into two or three flasks containing a solution of KOH and alcohol. The two or three flasks which form the condensing apparatus should be kept as cold as possible. The ruthenium is transformed into volatile RuO_4 which condenses in the flasks, while the iridium remains in the retort.

Separation of Ruthenium from Rhodium.—The mixed solution of the two metals is treated with potassium nitrite as described above. The orange-yellow solution is evaporated to dryness upon the water bath and treated with absolute alcohol. The rhodium remains undissolved and can be filtered off and washed with alcohol. The rhodium salt can be ignited with NH_4Cl and after washing yields metallic rhodium. See Separation of Rhodium from Ruthenium.

Separation of Ruthenium from Osmium.—The tetroxides from the chlorine distillation are caught in HCl. After heating to about 70° C., air should be drawn through the distillate for about half an hour to eliminate the osmium. See Separation of Osmium from Ruthenium.

[25] "Select Methods in Chemical Analysis," Sir Wm. Crookes.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF RUTHENIUM

Ruthenium is weighed as the residue or metallic ruthenium after it has been separated from the other metals.

The residue containing ruthenium or osmiridium is fused in a silver crucible with five grams KOH and one gram KNO_3 at a low temperature from one-half to one hour. The mass is cooled and extracted with water. The orange-colored solution containing potassium ruthenate is gently distilled in a current of chlorine whereby the volatile ruthenium tetroxide passes over into the receivers. All connections should be ground glass so that no Ru will be reduced in the joints. The solution in the distilling flask must be kept alkaline to prevent iridium chloride from distilling over with the Ru. Add a small piece of KOH after the first distillation and distill as before. Oftentimes it will be necessary to fuse again with KOH and KNO_3 and distill as stated above. Continue to pass chlorine through the alkaline solution until all effervescence ceases. Disconnect the chlorine and draw air through the apparatus, heating the solution nearly to boiling.

1. Receivers containing KOH solution (10 to 15% KOH) and alcohol.

a. This alkaline solution containing the ruthenium tetroxide distillate is evaporated to a smaller volume and the ruthenium is precipitated by boiling with absolute alcohol. Filter, wash well with hot water, dilute HCl and again with hot water. Ignite, reduce in hydrogen and weigh as metallic Ru.

b. The alkaline solution from the receivers is made acid with HCl and the Ru is precipitated from the hot solution with hydrogen sulfide gas. Filter, wash, ignite at a high temperature, reduce in hydrogen and weigh as metallic Ru.

2. Receivers containing hydrochloric acid.

a. This acid solution containing the ruthenium tetroxide distillate is heated to nearly boiling and the ruthenium is precipitated with hydrogen sulfide gas as under 1*b*.

b. The acid solution containing the Ru is evaporated to a concentrated solution and transferred to a weighed porcelain crucible. Evaporate to dryness, bake and ignite. Reduce in hydrogen and weigh as metallic Ru.[26]

c. Ruthenium may be estimated by precipitation with magnesium from solutions of its salts. The precipitate is washed with dilute sulfuric acid to remove excess of magnesium, dried, ignited in a current of hydrogen, cooled in carbon dioxide and weighed as metal.[27]

d. Evaporate to a moist residue on the steam bath. Add 10 ml. of HCl and digest the solution for one-half hour. Add 50 ml. of water and heat the solution to boiling in order to complete the dissolving of the somewhat difficultly soluble ruthenium compound. When the ruthenium compound is completely dissolved, filter the solution and wash the filter with diluted HCl (1 : 99). The solution is filtered to ensure the elimination of a small amount of silica which may be present. Dilute the ruthenium solution to 200 ml., heat it to boiling, and add a filtered 10% solution of sodium bicarbonate until a precipitate begins

[26] A correction should be made for impurities in the HCl used.
[27] Text Book of Inorganic Chemistry, Vol. IX, Part I. J. N. Friend.

to form. Add the bicarbonate solution dropwise until the acidity of the solution reaches a value of pH 6 as indicated by the change in color from yellow to blue of brom cresol purple indicator present in the solution. Boil the solution for 5 to 6 minutes and filter it.

Wipe the inner walls of the beaker and also the glass rod with a small piece of ashless filter paper. Thoroughly wash the filter and precipitate with a hot 1% solution of ammonium sulfate. Finally wash them 3 or 4 times with a cold 2.5% solution of ammonium sulfate.

Place the filter and precipitate in a porcelain crucible, dry them, and char the filter slowly. The dried filter will usually char completely when once it begins to smoke. This operation should be done carefully in order to prevent loss of ruthenium by deflagration. Ignite the residue strongly in air and then in hydrogen. Cool the resulting metal in hydrogen and leach it well with hot water. This is done to ensure complete removal of soluble salts. It is well to leach the residue in the crucible first and then to transfer it to a filter. Ignite the filter and metal in air and in hydrogen. Cool the residue in hydrogen and weigh it as metallic ruthenium.[28]

[28] Raleigh Gilchrist, Research Paper 654, J. Research Nat. Bur. Standards, 12, 1934.

RHODIUM

Element, Rhodium. **Rh.** *at.wt.* **102.91;** *sp.gr.* **12.5;** *m.p.* **1955° C.;** *oxides,* **RhO, Rh_2O_3, RhO_2**

DETECTION

Rhodium is found only in platinum ores. It is a white metal, difficultly fusible, and insoluble in acids. Rhodium, however, dissolves in aqua regia when alloyed with platinum, to a cherry red solution. It is also soluble in molten phosphoric acid and dissolves when fused with acid potassium sulfate with the formation of $K_3Rh(SO_4)_3$. If the metal is treated with chlorine in the presence of sodium chloride there forms a soluble salt, Na_3RhCl_6.

Rhodium monoxide, RhO, is obtained by heating the hydroxide $Rh(OH)_3$; by cupellation of an alloy of rhodium and lead, or by igniting the finely-divided metal in a current of air. It is a gray powder with a metallic appearance, and is not attacked by acids. When heated in hydrogen it is reduced with evolution of light.[29]

The oxide, Rh_2O_3, is obtained as a gray iridescent spongy mass by heating the nitrate. It is also formed as a crystalline mass when sodium rhodochloride is heated in oxygen. It is perfectly soluble in acids.[29]

Rhodium dioxide, RhO_2, is obtained by repeated fusions of the metal with KOH and KNO_3. It is attacked neither by alkalies nor by acids and is reduced by hydrogen only at a high temperature.[29]

Hydrogen sulfide precipitates rhodium sulfide, when passed into a boiling hot solution containing rhodium.

Potassium hydroxide precipitates at first a yellow hydroxide, $Rh(OH)_3 + H_2O$ soluble in an excess of the reagent. If boiled, a dark gelatinous precipitate separates. A solution of Na_3RhCl_6 does not show this reaction immediately, but the precipitate appears in the course of time. Addition of alcohol causes a black precipitate immediately.

Ammonium hydroxide produces a precipitate which dissolves in excess NH_4OH on heating. Addition of HCl now produces a yellow precipitate, insoluble in HCl but soluble in NH_4OH.

Potasium nitrite precipitates from hot solutions a bright yellow precipitate of double nitrite of potassium and rhodium.

Zinc, iron and formic acid precipitate rhodium as a black metal.

Hydrogen reduces rhodium salts.

To detect small amounts of rhodium in the presence of other metals, evaporate the solution and displace with a fresh solution of sodium hypochlorite; the yellow precipitate formed is soluble after an addition of acetic acid. After a long agitation the solution changes to an orange-yellow color

[29] "Treatise on Chemistry," Roscoe and Schorlemmer. The Macmillan Co.

and after a short time the color passes and finally a gray precipitate settles and the solution turns sky-blue.[30]

ESTIMATION

Rhodium is estimated mainly in ores, thermocouples and salts.

PREPARATION AND SOLUTION OF THE SAMPLE

When rhodium is estimated in thermocouples or other alloys of platinum and rhodium the wire or sample is rolled to a thin ribbon and dissolved in aqua regia. (An alloy containing 30% of Rh is practically insoluble in aqua regia.) Both metals will go into solution, forming the chlorides of rhodium and platinum. The aqua regia will have to be replaced from time to time, as the alloy dissolves slowly.

The rhodium from salts is precipitated with zinc and the black metallic rhodium cleaned with dilute aqua regia, filtered, washed, ignited and reduced with hydrogen. If platinum is present with the rhodium the residue will invariably contain a small amount of platinum after the aqua regia treatment. If all the platinum is desired it will be necessary to alloy with silver as described on page 731.

Some alloys and ores are alloyed with silver and the silver and platinum are dissolved in HNO_3. The residue is cleaned with aqua regia, dried, and weighed as metallic rhodium.[31] If the residue is ignited, reduce with hydrogen.

The material or residue containing rhodium is fused with $KHSO_4$, or better still $K_2S_2O_7$, for some time at a red heat and the mass leached with hot water acidified with HCl. The rose-red solution contains the rhodium. Several fusions are generally necessary.

SEPARATIONS

Separation of Rhodium from Platinum.—Alloys and ores containing platinum and rhodium dissolve slowly in aqua regia as stated above. After expelling the HNO_3 add NH_4Cl. The precipitate is filtered and washed with dilute ammonium chloride solution, which dissolves the rhodium salt. A very

[30] Prescott and Johnson.
[31] See Separations under Ir.

small amount of rhodium will color the filtrate pink to a rose-red color, depending on the amount of rhodium present. A green tinge in the ammonium chloroplatinate indicates the presence of rhodium.

A solution of NaOH is added to the HCl solution of the two metals until yellow rhodium hydroxide begins to separate. After neutralizing, the volume of the solution should be so adjusted that the estimated total content of Pt and Rh does not exceed 1 gram per 100 ml. A mixture of equal volumes of solutions containing 90 grams of crystallized barium chloride and 36 grams of anhydrous sodium carbonate per liter, respectively, is added. Not less than 5 ml. of each solution is taken. After the suspension of barium carbonate is added, the solution is rapidly heated to boiling and boiled for two or three minutes. The residue is filtered off and washed several times with a hot 2% solution of sodium chloride, after which it is returned, with the filter paper, to the original beaker and digested with 25 ml. HCl (1HCl to $4H_2O$) until solution is complete. Dilute with water and filter off the paper pulp. Adjust the volume to about 150 ml., heat to incipient boiling for 30 to 45 minutes while a current of hydrogen sulfide is passed in. After the precipitation the rhodium sulfide is filtered off at once, washed with water containing a little ammonium chloride, and ignited in a weighed porcelain crucible. The ignited sulfide is reduced and cooled in hydrogen, and weighed as metallic Rh.[32]

Separation of Rhodium from Iridium.—A separation can be made by adding sodium nitrite in excess to the solution of the two metals, with a sufficient quantity of sodium carbonate to make the solution neutral or alkaline; this is boiled until the solution assumes a clear orange color. The rhodium and iridium are converted into soluble double nitrites. A solution of sodium sulfide is added in slight excess and the liquid made slightly acid. The rhodium is precipitated as dark-brown rhodium sulfide.

A solution of rhodium and iridium is evaporated with HCl and displaced with a large excess of acid sodium sulfite, $NaHSO_3$, and allowed to stand sometime when a pale yellow double salt of rhodium and sodium sulfite slowly separates out while the solution becomes nearly colorless. Wash out the precipitate, and heat with hot concentrated H_2SO_4 till the sulfurous acid is driven off. Heat the material in a crucible until rid of all free sulfuric acid. Then the iridium is dissolved out as a sulfate with a deep chrome-green color, while a double salt of sodium sulfate and rhodium oxide remains behind. This is flesh color insoluble in water and acids. Boil with aqua regia, wash, dry, heat and the salt decomposes into rhodium and sodium sulfate.[33]

Rhodium can also be separated from iridium, when the latter is present as an iridic salt such as $Ir(SO_4)_2$, by precipitating the mixed salts with caustic potash, dissolving the hydroxides in dilute sulfuric acid and adding caesium sulfate. The sparingly soluble rhodium caesium-alum separates in the cold, and can readily be purified by recrystallization and then by electrolysis.[34]

The residue of rhodium and iridium is melted or scorified with test lead. The lead button is cleaned and dissolved in dilute HNO_3. After filtering and washing the residue, do not ignite, but wash the contents of the filter into a beaker and fume with H_2SO_4 from one to three hours. When cool, dilute with

[32] Edward Wichers, J. Am. Chem. Soc., 46, 1818 (1924).
[33] Handbuch der Anorganischen Chemie, O. Dammer. F. Enke, Stuttgart.
[34] "Treatise on Chemistry," Roscoe and Schorlemmer. The Macmillan Co.

water and let stand over night. The residue contains the iridium and a small amount of $PbSO_4$, while the solution contains the rhodium as the sulfate. To make a further separation from impurities present, the sulfate solution is made alkaline with NaOH and boiled. Let stand until cold and filter off the rhodium hydroxide. Digest with HCl until all the hydroxide has dissolved. Filter and wash with hot water. Evaporate the filtrate to dryness, dissolve in hot water and add about 15 ml. of sodium nitrite solution (40% $NaNO_2$). Heat until all action ceases, then add sodium carbonate to the hot solution until no more precipitate forms. Let cool, filter and wash with hot water. Acidify the filtrate with dilute acetic acid and add potassium chloride solution (20% KCl) until all the Rh is precipitated. Let stand over night at 50 to 60° C. When cold, filter the white precipitate, washing with 20% KCl solution containing a little $NaNO_2$. The white precipitate of potassium rhodium nitrite is digested with HCl, filtered and washed with hot water. Evaporate the HCl solution to dryness, add ammonium formate and heat until dry. Ignite, wash free from salts with hot water, reduce in hydrogen, cool in CO_2, and weigh as metallic Rh.

Separation of Rhodium, Platinum and Palladium.—Having the three in solution precipitate the platinum with NH_4Cl as described under Platinum. After filtering off the $(NH_4)_2PtCl_6$ precipitate, and after neutralizing the filtrate with Na_2CO_3 add mercuric cyanide to separate the palladium as $Pd(CN)_2$ as described under palladium. The filtered solution is evaporated to dryness with an excess of HCl. On treating the residue with alcohol, the double chloride of rhodium and sodium is left undissolved as a red powder. By heating this in a tube through which hydrogen is passed the rhodium is reduced to the metallic state and the sodium chloride is washed out with water leaving a gray powder of metallic rhodium.

The residue containing these three metals is scorified with test lead, and the resultant lead button cupelled with silver. The silver bead is dissolved in dilute HNO_3; the solution filtered, washed with hot water, ignited, and the residue treated with dilute aqua regia to dissolve any platinum or palladium that may be present. Filter, wash with hot water, ammonia water, and again with hot water. Ignite and reduce in hydrogen as metallic Rh.[35] (See Separations under Ir.)

Separation of Rhodium from Ruthenium.—The solution containing the two metals is treated with sodium nitrate as above and evaporated to dryness. The residue is powdered and treated in a flask with absolute alcohol. After filtering and washing with alcohol the rhodium remains undissolved.

The substance or residue containing the rhodium and ruthenium may be fused with $KHSO_4$ in a porcelain or platinum crucible causing the rhodium to go into solution as already described. The ruthenium remains insoluble.

See distillation of ruthenium.

[35] Very often this Rh contains lead in amounts varying from a trace to 35%.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF RHODIUM

1. The solution containing rhodium is treated with zinc and the residue is washed well with hot water acidulated with HCl. The residue is then cleaned with dilute aqua regia and the black metallic rhodium is filtered off, dried, and ignited in hydrogen. Cool and weigh as metallic rhodium.[36]

2. The rhodium solution containing about 5% free acid is treated for one-half to one hour with a rapid stream of H_2S while the solution is kept boiling on the hot plate. Let settle over night, filter, wash well with hot water, ignite, reduce in hydrogen, cool in CO_2 and weigh as metallic rhodium.

3. The solution containing the rhodium is made alkaline with KOH and then acid with formic acid, boil, and the rhodium will be precipitated as finely divided metallic rhodium. After filtering wash well with hot water, ignite, clean with dilute aqua regia and finish in the usual manner.

4. After the platinum and the palladium are eliminated, the residue of Ir, Rh and Ru is fused with $K_2S_2O_7$ in a porcelain crucible and the melt dissolved in water. Filter, wash with hot water, and after acidulating with HCl the Rh is precipitated with C.P. powdered zinc, hydrogen sulfide gas or both. Filter, wash with hot water and ignite. Clean the residue with dilute HNO_3, then with dilute aqua regia, wash with hot water, ignite in hydrogen and weigh as metallic Rh.[36]

5. The residue containing Ir, Rh, Ru and Os is fused with five grams KOH and one gram KNO_3, and the Ru and Os are distilled with chlorine as explained under ruthenium. The solution from the distilling flask is filtered, washed with water and the filtrate is made acid, zinced thoroughly, filtered, joined with the original residue and the whole ignited. The residue of impure Ir and Rh is scorified with test lead, the lead button dissolved in dilute HNO_3 and the residue treated with H_2SO_4 as explained under Separation of Rh from Ir. The clear rhodium sulfate solution is treated with C.P. powdered zinc, hydrogen sulfide gas or both, and the precipitate is treated as explained above and weighed as metallic Rh.[36]

6. The solution from the distilling flask is zinced well as explained above. The residue is filtered, washed, ignited and boiled with a few ml. of HNO_3 and then boiled with H_2SO_4 for one to three hours. Cool, dilute with three times its volume of water, filter and wash thoroughly with hot water. The rhodium sulfate solution is made alkaline with KOH and boiled with alcohol until all the rhodium is precipitated and the solution is clear. Filter, wash with hot water, dilute HNO_3 and again with hot water. Ignite, reduce in hydrogen and weigh as metallic Rh.

7. Rhodium is conveniently estimated by precipitation with magnesium from solutions of its salts. The precipitate is washed with dilute H_2SO_4 to remove excess of magnesium, dried, ignited in a current of hydrogen, cooled in carbon dioxide and weighed as metal.[37]

[36] This weight may be somewhat high due to contamination with Zn, as well as other impurities either from the solution or reagent.

[37] Text Book of Inorganic Chemistry, Vol. IX, Part I. J. N. Friend.

8. A solution containing the rhodium and iridium as chlorides, together with the excess of dimethylglyoxime remaining from the precipitation of palladium is placed in a 500-ml. Erlenmeyer flask. (See 6 under Gravimetric Methods for Palladium). Place a short-stemmed funnel in the mouth of the flask. Add 10 ml. of H_2SO_4 and 2 to 3 ml. of HNO_3, and evaporate until heavy vapors of H_2SO_4 are evolved. To ensure complete destruction of organic matter, add a small quantity of HNO_3 from time to time and continue to heat over a free flame, keeping the solution in constant motion. Dilute the cooled solution with 20 ml. of water and again evaporate it until vapors of H_2SO_4 appear. This is done to destroy nitroso compounds which may interfere in the precipitation of rhodium by titanous chloride.

Transfer the sulfate solution to a clean, unetched beaker, dilute it to 200 ml. and heat it to boiling. Add dropwise a solution of titanous chloride (a 20% solution of this reagent may be purchased) until the supernatant liquid appears slightly purple. If the solution is placed over a 100-watt light and stirred, observation of the end-point is greatly facilitated. The metallic rhodium which is precipitated quickly coagulates into a spongy mass. If much iridium is present, the end-point can be determined by the lack of formation of any further precipitate and the appearance of an orange color in the solution. Boil the solution for two minutes and filter it. Wipe the walls of the beaker and also the stirring rod with a piece of ashless filter paper. Wash the filter and precipitated metal thoroughly with cold (room temperature) diluted H_2SO_4 (2.5 : 97.5).

Place the filter with its contents in a 500-ml. Erlenmeyer flask, add 10 ml. of H_2SO_4, char gently, add 5 ml. of HNO_3, and digest the solution on a hot plate. Usually, the rhodium dissolves fairly readily. Complete the solution of the rhodium by heating the flask over a free flame, keeping the contents of the flask in constant motion. Ensure the destruction of organic matter and the elimination of nitroso compounds. If some black specks remain, dilute the solution, filter it and return the filter to the flask. Wipe down the walls of the flask with a piece of ashless filter paper. Add 5 ml. of H_2SO_4, char the paper, and destroy all organic matter with HNO_3. Heat the solution until heavy vapors of H_2SO_4 are evolved. This treatment will dissolve any remaining metal and will leave only a slight deposit of colorless silica.

Precipitate the rhodium a second time in the manner described above. Redissolve the rhodium as before, dilute the H_2SO_4 solution with 20 ml. of water and 10 ml. of HCl and boil the resulting solution for fifteen minutes. This treatment is necessary to convert the rhodium into a form which will allow complete precipitation by hydrogen sulfide. During this treatment, the color of the solution will change from yellow to rose. Filter the solution and wash the filter with diluted HCl (1 : 99). Finally, dilute the solution to a volume of from 400 to 500 ml.

Precipitate the rhodium with H_2S as directed under 2. Filter the solution and wash the precipitate with diluted H_2SO_4 (2.5 : 97.5), and finally with diluted HCl (1 : 99). Place the filter with the sulfide precipitate in a porcelain crucible. Ignite the dried precipitate carefully in air. Finally, ignite the oxidized residue in hydrogen, cool the resulting metal in hydrogen and weigh it as metallic rhodium.[38]

[38] Gilchrist and Wichers, J. Am. Chem. Soc., 57, 2565 (1935).

OSMIUM

***Element, Osmium.* Os. *at.wt.* 191.5, *sp.gr.* 22.4; *m.p.* 2700° C.? *oxides,* OsO, Os_2O_3, OsO_2, OsO_4**

DETECTION

Osmium occurs with platinum ores as a natural alloy with iridium (Osmiridium) and remains undissolved in the form of hard, white metallic-looking grains when the ores are treated with aqua regia. The chlorides, $OsCl_2$ and $OsCl_4$, combine with the alkali chlorides. Through the action of HNO_3, aqua regia or heating in a stream of moist chlorine, osmic tetroxide is formed. OsO_4 is very volatile and the fumes are poisonous. It is detected readily by the odor when heated, as the fumes are highly corrosive and disagreeable like chlorine. Chlorine passed over hot osmium mixed with KCl gives K_2OsCl_6, which dissolves in cold water.

The oxy-hydrogen flame oxidizes the metal but does not melt it. When strongly heated in contact with air, the finely divided osmium burns and is converted into OsO_4, commonly called osmic acid.

Osmium monoxide, OsO, is obtained when the corresponding sulfite mixed with sodium carbonate is ignited in a current of carbon dioxide. It is a grayish-black powder insoluble in acids.[39]

The oxide, Os_2O_3, is a black insoluble powder obtained by heating its salts with sodium carbonate in a current of carbon dioxide.[39]

Osmium dioxide, OsO_2, is obtained from its salts in a similar way to the foregoing oxides. It is likewise formed when its hydroxide is heated in a current of carbon dioxide.[39]

Osmium tetroxide, OsO_4. Very finely-divided metallic osmium oxidizes slowly at the ordinary temperature, and at about 400° C. takes fire with formation of OsO_4. The denser the metal the higher is the temperature needed for oxidation.[39]

Hydrogen sulfide precipitates dark brown osmium sulfide, OsS_2, but only in the presence of some strong mineral acid; from an aqueous solution of osmic acid there forms a dark brownish-black sulfide, OsS_4. These are insoluble in ammonium sulfide.

Potassium hydroxide precipitates reddish-brown osmium hydroxide, $Os(OH)_4$.

Ammonium hydroxide precipitates the osmium hydroxide.

Zinc and formic acid precipitate black metallic osmium.

Hydrogen reduces osmium compounds to the metal.

Potassium nitrite added to a solution of osmic acid reduces it to osmous acid which unites with an alkali forming a beautiful red salt.

Sodium sulfite yields a deep violet coloration and a dark blue osmium sulfite separates out gradually.

[39] "Treatise on Chemistry," Roscoe and Schorlemmer. The Macmillan Co.

Phosphorus reduces osmium from an aqueous solution.[39]

Mercury precipitates osmium from an aqueous solution of osmic acid mixed with HCl.

Stannous chloride produces a brown precipitate, dissolving in HCl to give a brown fluid.

B-naphthalamine hydrochloride produces a blue color when reacting with a sodium or potassium osmate solution. This is a delicate and characteristic test which can be used in the presence of ruthenium.[40]

Thiourea, $CS(NH_2)_2$, when added to a solution containing OsO_4 or K_2OsCl_6 acidified with a few drops of HCl and heated for a few minutes, causes a deep red or rose color to appear.[41]

ESTIMATION

Osmium is estimated mainly in osmiridium, synthetic alloys for pen-point material, spark points and platinum residues.

PREPARATION AND SOLUTION OF THE SAMPLE

After the platinum is extracted the residue or osmiridium is mixed with two or three times its weight of common table salt. The mixture is put in a porcelain or silica tube and heated to a dull red heat; moist chlorine is then passed through the tube and thence through receivers containing KOH and C_2H_5OH to catch the Os and Ru that pass over. The mass is cooled and dissolved with water. After several treatments the entire group of platinum metals will be in solution.

The osmium material may also be fused with KOH and KNO_3 and the melt dissolved in water. The osmium will be in solution as potassium osmate, K_2OsO_4, while the iridium remains as residue.

Cold selenic acid has no appreciable action on osmium; at about 120° C., however, the metal is dissolved to a colorless solution which contains selenious acid and OsO_4, but no selenate.[42]

[40] Ogburn and Miller, J. Am. Chem. Soc., 52, 42, 1930.
[41] L. Chugaev, Compt. rend., 167, 235, 1918.
[42] K. Hradecky. See C. A., 12, 657 (1918).

SEPARATIONS

In most cases osmium is separated from the other metals present by distillation or volatilization. See Gravimetric Methods.

GRAVIMETRIC METHODS FOR THE DETERMINATION OF OSMIUM

The osmium is very difficult to ascertain on account of the element being very volatile.

1. The potassium osmate, K_2OsO_4, solution is put in a small retort and boiled with HNO_3, the OsO_4 is conducted into receivers containing NaOH solution and C_2H_5OH. The osmate solution from the receivers is heated gently and strips of aluminum are plunged in; the osmium will be deposited in metallic form, while the aluminum dissolves in the soda. Care must be taken not to add too much aluminum, as an aluminate might be precipitated which is troublesome. When the solution is decolorized, the dense precipitated osmium is washed by decantation with water to remove the sodium aluminate, and then with 5% H_2SO_4 solution to remove the excess aluminum. The osmium is dried in a bell-jar filled with hydrogen, then heated to a dull redness and cooled in a current of hydrogen. The osmium is weighed as the metal. As a check the osmium may be driven off in the form of OsO_4 by heating to redness with plenty of air, or better, in a current of oxygen and weighing again.[43]

2. The osmate solution from the condensing receivers or from the fusion of KOH and KNO_3 containing the ruthenium and osmium is placed in a retort and HCl is added. A slow current of air or oxygen is passed through the retort and thence through receivers containing KOH and alcohol similar to the ones mentioned above. These receivers are kept as cold as possible. The osmium is distilled over as OsO_4 while the ruthenium remains in the retort. Combine the solutions in the receivers and proceed to determine the osmium as described.

3. The potassium or sodium osmate solution from the receivers above or where osmium tetroxide is dissolved in potassium hydroxide solution and alcohol is heated at 40 or 50° C. to form potassium osmate. A slight excess of dilute sulfuric acid is added and then 10 ml. more of alcohol in order to prevent reoxidation. After ten or twelve hours, a bluish-black deposit settles, while the supernatant liquid is colorless and free from osmium. The precipitate is filtered, washed with aqueous alcohol, and converted into metallic osmium by reduction in a current of hydrogen.

[43] "Select Methods of Chemical Analysis," Sir Wm. Crookes. Longmans, Green & Co.

4. The residue containing osmium is fused with five grams KOH and one gram KNO_3 in a silver crucible as explained under ruthenium. Add HNO_3 slowly to the distilling flask which is connected to receivers containing NaOH solution and alcohol (10% NaOH and 10% C_2H_5OH). Draw the distillate over gently with the aid of the vacuum, the same as for the chlorine distillation under ruthenium. Continue the HNO_3 until strongly acid and then boil for a short time. Transfer the alkaline solution containing the OsO_4 distillate to a beaker and pass in hydrogen sulfide gas while the solution is heating until saturation; then add HCl until the solution is distinctly acid and continue to saturate the hot acid solution with hydrogen sulfide gas. Let stand over night, filter through a weighed Gooch crucible, washing well with hot water. Ignite in hydrogen, cool in CO_2 and weigh as metallic Os.

NOTES.—The ignition of the sulfide precipitate in hydrogen leaves the osmium containing some sulfur. A correction can be made, however, by dissolving the residue in aqua regia and precipitating the sulfur with barium sulfate.

The hydrogen used in the reduction of the osmium should be displaced with CO_2 before the air is admitted, to prevent explosion caused by the catalytic action of the metal.

After the osmium is removed with HNO_3 as described above, the ruthenium can be distilled after making the contents of the flask alkaline with KOH. Proceed then as described under the distillation of ruthenium.

5. The sodium osmate solution from the receivers above is treated with concentrated HCl until slightly acid. Heat to the boiling point to change the sodium osmate to sodium chlorosmate. An excess of a saturated aqueous solution of strychnine sulfate is added and warmed on the water bath to coagulate the canary-yellow precipitate. Filter immediately through a prepared Gooch crucible and after washing thoroughly with warm water to remove the chlorides, dry at 105° C. Weigh as $(C_{21}H_{22}O_2N_2)_3Os$ and calculate the percentage of Os in the salt, using the empirical factor 0.1758.

The other platinum metals also precipitate with strychnine sulfate, but that of ruthenium is soluble in boiling 95% ethyl alcohol. This affords a ready method of separating osmium from ruthenium. Precipitate both metals with a small excess of a saturated solution of strychnine sulfate and add an equal volume of 95% ethyl alcohol. Boil the mixture until the precipitates dissolve. Upon cooling, the osmium compound reprecipitates and after standing for one and one-half hours, is filtered through a prepared Gooch filter as explained above.[44]

6. The osmium is distilled from the distilling flask as OsO_4 by adding HNO_3 as described above. The distillate is caught in receivers containing 150 ml. of dilute HCl (1 : 1), freshly saturated with SO_2, in the first receiver, and 50 ml. of the same reagent in each of the other two absorbing flasks.

Unite the portions of the absorbing solution and evaporate as far as possible on the steam-bath in a clean, unetched beaker. It is important, in precipitating the platinum metals hydrolytically, that the beakers used do not have an etched surface. An etched beaker often becomes stained with the precipitate, and this stain cannot always be removed readily. Digest the residue with 10 ml. of HCl for fifteen minutes, and evaporate a second time. Repeat the

[44] S. C. Ogburn, Jr. and L. F. Miller, J. Am. Chem. Soc., 52, 42, 1930.

digestion with HCl and the evaporation three times more. This is done to ensure complete decomposition of any sulfite compounds of osmium. Dissolve the residue from the last evaporation in 150 ml. of water. Heat the resulting solution to boiling, and add to it a filtered 10% solution of sodium bicarbonate until a precipitate appears and suddenly coagulates. Add a few drops of brom phenol blue indicator solution (0.04%) to the hot solution. This indicator changes from yellow to blue at pH 4. Add the bicarbonate solution dropwise until the indicator assumes a faint bluish color. Finally, boil the solution from five to six minutes to ensure complete precipitation of the hydrated osmium dioxide.

Filter the solution through a Munroe platinum crucible, carefully pouring the supernatant liquid through first. Transfer the precipitate, and wipe the inner walls of the beaker and also the glass rod with a rubber policeman which has been thoroughly wetted so that the precipitate will not cling to it. It should be borne in mind that filter paper must not be used to wipe the beaker, although it is used when handling precipitates of any of the other five platinum metals. Wash the precipitate thoroughly with a hot 1% solution of ammonium chloride, and then cover it with solid ammonium chloride. Moisten the ammonium chloride with a few drops of the wash solution and saturate the precipitate by applying suction. If desired, a saturated solution of ammonium chloride may be used to impregnate the precipitate. Continue the suction until the bottom of the crucible is coated with solidified ammonium chloride. Wipe off this coating of salt and place the platinum cap on the bottom of the crucible.

Cover the crucible with a Rose lid, preferably of quartz. Ignite a stream of hydrogen from a Rose delivery tube, likewise of quartz, and regulate the stream so that a very small flame is produced. Then insert the tube through the opening in the lid. The hydrogen flame will probably become extinguished by this operation and must be reignited. This is done by momentarily placing a burner flame under the crucible. The hydrogen will now burn as it emerges from under the lid at the edge of the crucible. The ignited hydrogen generates the requisite amount of heat to dehydrate the osmium compound without causing deflagration. After five minutes, gradually heat the crucible with the burner flame until all of the ammonium chloride is expelled. Ignite the osmium residue strongly in hydrogen for ten minutes. Remove the burner and allow the crucible to cool somewhat. Extinguish the hydrogen flame by momentarily breaking the current of hydrogen, and allow the crucible to cool to room temperature. Finally, displace the hydrogen with a current of CO_2, without even momentary access of air. If the hydrogen is not displaced by an inert gas, such as CO_2, the reduced metal will be rapidly attacked when first exposed to the air, with significant loss of osmium. Weigh the residue as metallic osmium.[46]

[46] Gilchrist and Wichers, J. Am. Chem. Soc., 57, 2565 (1935).

[illegible] OF PLATINUM METALS[1]

	Ruthenium ($RuCl_3$)	Rhodium ($RhCl_3$)	Palladium ($PdCl_2$)	Osmium ($OsCl_4$)	Iridium ($IrCl_4$)	Platinum ($PtCl_4$)
Color[2]	Dark brown	Red	Brownish yellow	Yellow	Dark brown	Yellow
Hydrogen[2] sulfide at 80° C.	Azure-blue color on prolonged treatment	Brownish black ppt., Rh_2S_3	Brownish black ppt., PdS	Brownish black ppt., OsS_2	Brownish black ppt., Ir_2S_3	Brownish black ppt., PtS_2
Ammonium sulfide	Dark brown ppt., difficultly soluble in excess	Dark brown ppt., Rh_2S_3, insoluble in excess	Black ppt., PdS, insoluble in excess	Dark ppt., insoluble in excess	Brown ppt., Ir_2S_3, soluble in excess	Brown ppt., PtS_2, soluble in excess to $(NH_4)_2PtS_3$
Caustic alkalies	Black ppt. of hydrated oxide insoluble in excess	Yellow-brown ppt., $Rh(OH)_3$, soluble in excess	Yellowish brown basic salts soluble in excess	Brownish red $OsO_2 \cdot 2H_2O$	Green solution Brownish black double chloride ppt.	Dark ppt. of $PtO_2 \cdot xH_2O$
Ammonium[2] hydroxide on warming	Greenish coloring	Slow decolorization	Decolorized	Yellowish brown ppt.	Bright color	Slow decolorization
Saturated[2] NH_4Cl solution	Brown ppt.	No ppt.	No ppt.	Red ppt.	Black ppt.	Yellow ppt., $(NH_4)_2PtCl_6$
Saturated KCl solution	Violet cryst. ppt. of K_2RuCl_5	Red cryst. ppt., K_2RhCl_5	Red ppt. of K_2PdCl_4	Brown cryst. ppt., K_2OsCl_6	Brownish red ppt. of K_2IrCl_6	Yellow ppt. K_2PtCl_6
KI solution[2] (1 : 1000)	No change	No change	Dark ppt.	No change	Yellow color	Slow red-brown color
$Hg(CN)_2$ solution	No change	No change	White ppt., $Pd(CN)_2$	No change	No change	No change
KCNS, 1% solution	Dark violet color	Yellow color	Unchanged	Unchanged	Decolorized	Increased yellow color
Hydrazine in hydrochloric[2] acid solution	Yellow color	Yellow color	Black ppt., metallic Pd	No change	Yellow color	Black ppt., metallic Pt
Dimethyl[2] glyoxime	No change	No change	Yellow ppt.	No change	No change	No change
Metallic zinc	Ppt., Ru	Ppt., Rh	Ppt., Pd	Ppt., Os	Ppt., Ir	Ppt., Pt

[1] Textbook of Inorganic Chemistry, Vol. IX, Part I. J. N. Friend.
[2] With the platinum-metal salts in dilute solution. Based on the results of Mylius and Mazzucchelli, Z. anorg. allgem. Chem., 89, 1, 1914.

DETERMINATION OF IRIDIUM, PALLADIUM, PLATINUM AND RHODIUM IN DENTAL GOLD ALLOYS[46]

The alloys are usually in the form of wires, bands or plates. These should be rolled out to a ribbon or sheet .003 to .005 inch thick. These rolled pieces are then clipped to short lengths or small squares one-sixteenth to one-eighth of an inch in size.

A sample of .5 gram to 2 grams is taken at random from these small pieces, and dissolved at a low temperature in about 25 ml. of dilute aqua regia (1 part aqua regia to 1 part H_2O) in a 250 ml. beaker. Silver chloride will remain as an insoluble residue, which should be broken up from time to time with a glass rod until the alloy is completely decomposed. Add 150 to 200 ml. of water and digest for about an hour. Set aside to cool until the supernatant liquid is perfectly clear, when the silver chloride is filtered off, washed well with water, and hot dilute NH_4OH (1 part NH_4OH to 1 part of H_2O) is poured on the paper in successive portions until no more of the silver chloride can be seen. The iridium will be left on the paper as a black metallic residue. The platinum and palladium that were present will be in solution with the silver chloride. After washing the paper and iridium residue several times with hot 1% NH_4OH, place the paper and residue in a small beaker, add 15 to 25 ml. of dilute NH_4OH, and digest for half an hour. Filter through a small paper and wash well with hot 1% NH_4OH. Transfer the paper and residue to a weighed porcelain crucible for the determination of iridium. This residue is ignited in air to burn off the paper, then reduced in hydrogen and weighed as metallic iridium.

When the weight of the residue amounts to not more than .2 or .3% of the sample, the amount of platinum that is with the iridium is so small that it may be neglected. When larger amounts of iridium are present it is usually necessary to separate the platinum in the residue from iridium. (See page 733—Method of Deville and Stas, Modified by Gilchrist.)

Unite the two ammoniacal filtrates and acidify with HNO_3 to re-precipitate the silver chloride. This is filtered off and washed well with warm water. The filtrate is evaporated to dryness and cautiously add HCl, and again evaporate the residue to a small volume and transfer to a porcelain crucible where the residue is evaporated to dryness. Add about 10 grams of sodium pyrosulfate and fuse the mixture for about a half hour at a red heat, cool, and dissolve the melt in hot water. Pass H_2S through the solution for about a half hour while it is heated to incipient boiling on the hot plate. Filter off the platinum and palladium sulfides, wash and ignite to metal in a porcelain crucible. Dissolve the residue in the crucible in a few ml. of dilute aqua regia, filter off any silica, and add the solution to the main portion of the samples before the determination of platinum or palladium is made. If the original alloy contains no tin the above solution is evaporated to dryness and taken up with a little water followed by 10 ml. HCl. Dilute to about 200 ml., add about 50 ml. of a saturated solution of SO_2 in water and digest for about an hour. Additional SO_2 solution (10 to 20 ml.) is added and the solution is set aside to cool. The supernatant liquid is poured through a tight paper which has been

[46] William H. Swanger, Bureau of Standards. Scientific Papers of the Bureau of Standards, No. 532. 1926.

treated with filter paper pulp. Wash the gold thoroughly in the beaker by decantation with a hot 1% solution of HCl. The paper is washed thoroughly and together with the small amount of gold caught on it, is returned to the beaker. This gold precipitate is dissolved in 20 ml. of dilute aqua regia, filtered and washed with hot 1% HCl. The solution is then evaporated to dryness at a low temperature. Take up with 2 or 3 ml. HCl and again evaporate to dryness. Repeat until HNO_3 is eliminated. The residue is taken up with 5 ml. HCl, 8 to 10 drops H_2SO_4 and 150 ml. H_2O. Fifty ml. of a saturated solution of oxalic acid is added and the solution is boiled for not more than 15 minutes as prolonged boiling will precipitate some of the platinum or palladium. Ten ml. more of the oxalic acid is added and the solution is boiled for a minute or two, then is set on the steam bath for not less than four hours. Filter off the gold precipitate on a paper that has been treated with filter-paper pulp. Wash the beaker and the paper with the gold precipitate thoroughly with hot water.

The filtrate is evaporated to dryness, 5 ml. H_2SO_4 is added and again evaporated on the hot plate until nearly all the H_2SO_4 has been driven off. The oxalic acid will thus be eliminated.

The residue is digested with 10 ml. dilute aqua regia until all of the precipitated metals are again dissolved. The solution is filtered off from any silica (from the glassware) and added to the filtrate from the first precipitation of the gold. This solution is evaporated to dryness at a low temperature and the residue is digested with 10 ml. dilute aqua regia until all of it is in solution. Dilute to about 250 ml. and cool to room temperature. Enough of a 1% solution of dimethylglyoxime in alcohol is added to precipitate all of the palladium. The solution must not be heated as some of the platinum may be precipitated. After standing for one hour the precipitate is filtered off on a paper of suitable size and washed well with hot water. Additional reagent is added to the filtrate to ascertain whether or not all of the palladium has been precipitated. The precipitate with the paper is returned to the beaker and dissolved, on the steam bath, in 25 ml. of dilute aqua regia. The paper pulp is filtered off, washed with hot water, and ignited in a porcelain crucible. Any metallic residue is dissolved in the crucible with a few ml. of dilute aqua regia and the solution is added to the main solution of the palladium. This solution is diluted to about 250 ml. and the palladium is precipitated as before. The precipitate is filtered on a Gooch crucible, washed thoroughly with hot water, dried at 110° C., and weighed. The weight of the precipitate multiplied by .3167 gives the weight of palladium.

The precipitate can be filtered on a paper, and after washing and allowing to drain, the paper with the precipitate is removed from the funnel and carefully wrapped in another ashless filter paper. The whole is placed in a porcelain crucible and dried at a temperature not exceeding 110° C. Heat gently in hydrogen to decompose the compound. Ignite the paper in air and the residue is reduced to metallic palladium by heating strongly for several minutes in an atmosphere of hydrogen, and letting it cool very gradually. Weigh as metallic palladium.

The filtrates from the precipitation of palladium are united and evaporated to dryness. The excess of dimethylglyoxime is destroyed by adding about 5 ml. HNO_3 and digesting on the steam bath. The solution is again evaporated

to dryness and the residue digested with 10 ml. HCl and enough water to dissolve the salts present.

The copper is precipitated at this time as cuprous thiocyanate. Palladium shows some tendency to contaminate the precipitate of cuprous thiocyanate. For this reason it is recommended that palladium be separated before the determination of copper is made. If the cuprous thiocyanate is contaminated with platinum the precipitate should be dissolved and reprecipitated.

The filtrate or filtrates from the precipitation of copper is evaporated to dryness. The excess of thiocyanate is destroyed by adding 5 to 10 ml. HNO_3 and digesting the mixture at a low temperature for about half an hour. The solution is again evaporated to dryness. The HNO_3 is completely expelled by heating the residue on the hot plate with 5 or 10 ml. H_2SO_4 until fumes of H_2SO_4 appear. The residue is cooled and digested with 29 ml. of dilute HCl. The solution is finally diluted to about 100 ml. and boiled to put all of the platinum compounds in solution. The solution will usually contain a small amount of silica. This is filtered off and ignited in a porcelain crucible. The residue is leached with dilute aqua regia to dissolve the small amount of platinum it usually contains. This solution is evaporated separately to expel the HNO_3 and is then taken up with HCl and added to the main solution containing the platinum. This solution contains the platinum as well as rhodium and impurities.

Precipitate the platinum and the rhodium with H_2S as described before. If rhodium is absent the platinum sulfide is filtered off, ignited to metal and weighed as platinum.

When great accuracy is desired, this ignited sponge is dissolved in 10 ml. of dilute aqua regia and the solution is evaporated to dryness on the steam bath. HNO_3 is expelled by adding 2 or 3 ml. HCl and repeating the evaporation to dryness. The residue is taken up with 20 ml. of dilute HCl and 2 or 3 ml. H_2SO_4. The solution is diluted to about 300 ml. and the precipitation of the platinum with H_2S is repeated. In this way any error due to the presence of alkali salts in the first precipitate is eliminated.

If rhodium is present the sulfides of platinum and rhodium are filtered off and ignited, first in air, then in hydrogen, and weighed as metallic platinum plus rhodium.

The weighed sponge is transferred to a beaker and digested on the steam bath with 15 to 20 ml. of aqua regia. A little of the acid should be poured into the crucible in which the sponge was ignited to dissolve any metal adhering to the walls. The sponge generally dissolves completely. If there is a residue the solution is poured off and the residue is washed by decantation. Fresh portions of acid are added until it is certain that no more of the residue will dissolve. The residue may be considered to be rhodium. It is filtered off and ignited in the weighed porcelain crucible that is to be used for the determination of rhodium.

The solution of platinum and rhodium is evaporated nearly to dryness to expel most of the excess acids and is then diluted to about 200 ml. The free acid in the solution is neutralized with sodium hydroxide solution, using 4 to 8 drops of a .4 solution of cresol red as indicator. The alkaline color of the indicator need not persist for more than a few seconds. A freshly prepared mixture consisting of 5 ml. of a solution containing 90 grams of crystallized

barium chloride per liter, and 5 ml. of a solution containing 36 grams of anhydrous sodium carbonate per liter is added to precipitate the rhodium. After the suspension of barium carbonate is added the solution is rapidly heated to boiling and boiled for two minutes. The residue is filtered off, washed several times with a hot 2% solution of sodium chloride, returned, together with the paper, to the beaker, and digested with 25 ml. HCl (1 part HCl and 4 parts H_2O) until solution is complete. The presence of barium carbonate with the rhodium hydroxide may be noted by the evolution of CO_2 when the acid is added. If no barium carbonate is present the platinum-rhodium solution should be given a second treatment. If the first precipitate contains barium carbonate the filtrate may be acidified with HCl and set aside for the subsequent recovery of platinum.

After the mixture of barium carbonate and rhodium hydroxide has dissolved in HCl, the solution is diluted somewhat and filtered from the paper pulp. The solution is again treated with barium carbonate exactly as before. Care should be taken not to add an excess of NaOH in the preliminary neutralization. If the amount of rhodium present is very small, it is better to leave the solution slightly acid before adding barium carbonate. The period of boiling should be extended to three minutes. The precipitate is handled as before and a third precipitation made if desired. For mixtures of platinum and rhodium containing 1% or less of rhodium, two precipitations should be sufficient, unless the first precipitate was for some reason unduly contaminated with platinum.

The final solution of rhodium chloride and barium chloride is diluted to about 150 ml. It contains about 5 ml. HCl. Rhodium is precipitated as sulfide by passing a fairly rapid stream of H_2S for 30 to 45 minutes while the solution is heated to incipient boiling on the hot plate. The precipitated rhodium sulfide should be filtered off at once. If the solution is allowed to stand for some time after precipitation is completed, some of the barium present may be converted to sulfate and be included with the rhodium sulfide. The precipitate is washed with a hot 1% solution of NH_4Cl. The filtrate and wash water are discarded. The precipitate and paper are ignited in the crucible containing the insoluble residue from the solution of the mixed platinum-rhodium sponge. The ignited sulfide is finally reduced and cooled in an atmosphere of hydrogen. The residue is weighed as metallic rhodium. It should have a clean, light-gray color. The weight of rhodium thus obtained is subtracted from the weight of the mixed sponge of platinum and rhodium to get the weight of platinum in the sample.

The determination of Ag, Sn, Au, Cu, Zn, Ni, Mn, Fe and Mg have been omitted. If these metals are desired, consult the original Scientific Paper.

RADIUM [1]

Ra, *at.wt.* 226.05; *m.p.* about 700° C.; *half life period* 1600 yr.; *chloride* $RaCl_2$

OCCURRENCE

Belgian Congo, Africa—pitchblende, torbnerite, curite and kasolite; Western Colorado and Eastern Utah—carnotite; Canada—pitchblende. An early source of radium was pitchblende from Joachimsthal, Czechoslovakia; the Curies discovered radium in this ore.

DETECTION

Radium and other radioactive elements are detected by means of the electroscope. They may be detected also by use of the photographic plate. Radium is distinguished from the others by the half period of radon which it gives off.

ESTIMATION

Radium is usually estimated by its rate of discharging a calibrated or standardized electroscope. Alpha particles, beta particles, and gamma rays from radioactive substances ionize the air.

Methods.—Radium is determined by the following methods: I, Alpha Ray; II, Radon; III, Gamma Ray. The alpha ray method is only approximate. The samples should be as nearly in the same physical condition as possible and should be of nearly the same general composition as the standard

[1] By L. D. Roberts, Professor of Physical Chemistry, University of Southern California.

used. This method is used in the mining camps because it is simple and requires very little equipment.

The radon method being more accurate is used in the technical and scientific laboratories. The gamma ray method is used when the sample cannot be removed from the container, and also for very high grade material. Tubes of radon and radium salt prepared for therapeutic use are determined in this way.

The Lind instruments distributed by the Denver Fire Clay Company of Denver, Colorado, are very satisfactory for radium determinations.

Alpha Ray Instruments.—Radium in an ore can be approximately determined by the use of an alpha ray instrument. The Lind interchangeable head *A* is placed on the Alpha chamber, *B* (See Fig. 88). Head *A* contains an

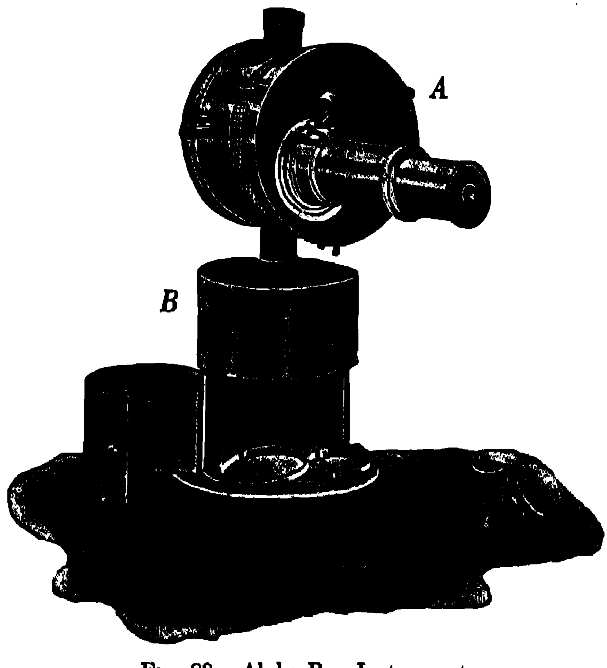


FIG. 88. Alpha-Ray Instrument.

aluminum or gold leaf attached to a metal rod, and a reading telescope so placed as to read the deflection of the leaf when charged. *B* is a chamber to receive the sample. A spring attached to the metal rod in *A* connects with a rod which extends into *B*. The lower extremity of the rod in *B* is attached to a metal disc. The rod in the chamber is insulated from the case with amberoid. The leaf is charged by means of a battery (small B batteries in series are good). From 300 to 400 volts are required. This will depend on the size of the leaf. The leaf may be charged by transforming the 110 volt A.C. current and passing through an electron tube or simply with an ebonite rod. It is best to ground the negative end and connect case *B* to ground and touch rod leading to leaf with a floating terminal from the positive side. In

order to have smaller steps a few ordinary dry cells can be used at the positive end. The positive wire can thus be attached where it will give the proper deflection to the leaf. A tube of distilled water is placed in the circuit to prevent shorting the system. The leaf should not be charged enough to throw it against the case for this may change the standardization of the instrument when the head is used on the various radon chambers. The "natural leak" is found by taking the time for the leaf to discharge through forty small divisions—from 8 to 4—and calculating the divisions per second. The sample is placed in the plate for solids, and this is made exactly full. The plate containing the sample is placed in a pan to protect the instrument from receiving active matter. The pan with its contents is placed within chamber *B*. With a stop watch the time of discharge of the leaf from 8 to 4 is taken. This represents forty small divisions. The rate of discharge is calculated in divi-

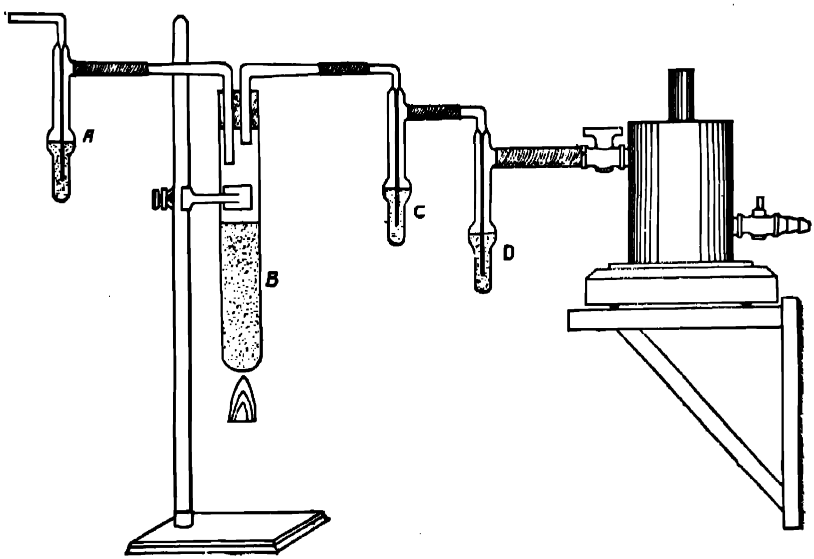


FIG. 89. Apparatus for the Radon Method.

sions per second, and the natural leak is subtracted. A standard is run in exactly the same way. Since the rate of discharge is directly proportional to the amount of radium present, the amount of radium in the sample is found by comparing its rate of discharge with that of the standard. This method gives approximate results. If the samples are of the same general character, the results may be in very good agreement, checking those obtained by the radon method very closely.

Radon Method. Bisulfate Fusion.—This method is accurate and is quite easily carried out. A pyrex test tube 30 mm. in diameter and 200 mm. long is filled about ¼ full of fused potassium bisulfate. Sodium bisulfate or a mixture of potassium and sodium bisulfates may be used. From 0.05 to 5 grams of the finely ground sample should be added, the amount depending upon the radium content of the sample. Care should be taken not to allow the sample to stick on the side of the tube. The sample may be weighed on a small filter paper, the paper folded around the sample and added to the tube.

More bisulfate (enough to make the tube about 1/3 full) is added in such a way as to carry down any sample sticking to the sides of the tube. The mixture is now thoroughly fused. The tube is removed from the flame and held in a nearly horizontal position and slowly rolled while the melt solidifies. This leaves the fused mass on the sides of the tube with a hole extending nearly to the bottom. Later when heating the tube it will not break. About 1/4 gram of barium carbonate is dropped into the tube. As soon as the tube is cool enough to be handled a rubber stopper carrying two glass tubes drawn out to rather fine tips is inserted (See Fig. 89). If this is done as soon as possible

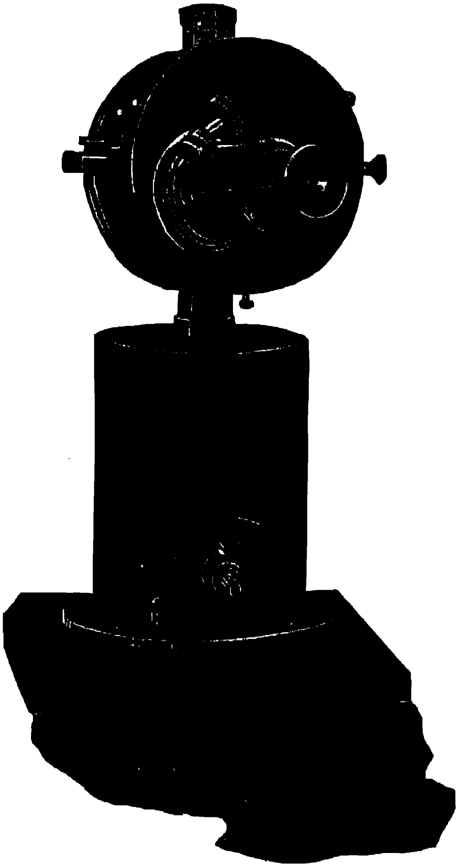


FIG. 90. Apparatus for Radium Determination.

there will be a partial vacuum in the test tube when it cools and will indicate when the radon is taken off that there have been no leaks. One of the tubes should extend about one-fourth of the way down the test tube and the other just through the stopper. After the radon has recovered at least one day the tube is connected to an evacuated chamber as shown in Fig. 90. The chamber may be evacuated by means of an aspirator or a pump. Microdrying bulb *A* contains water or sulfuric acid and serves as an indicator to show when the current of air into the chamber is correctly regulated. *B* contains the fused material; *C* sodium hydroxide solution; *D* sulfuric acid. The stopcock con-

nected to A by rubber tubing is opened very slightly until bubbles come through C and D very slowly. The tip near A is broken under the rubber tubing with a pair of pliers. On account of the vacuum in B, air bubbles through A. Immediately after breaking the first tip the second should be broken. The stopcock of the chamber is slowly opened until air bubbles steadily but not too fast through A. Heat is applied by a Meeker burner as soon as the tips are broken, and continued till the fusion has boiled for five minutes and then till the chamber is at about atmospheric pressure. It may be necessary to use a blast lamp in conjunction with the other burner. The fused mass must be boiled. During the heating, a steady current of air is maintained by regulating the stopcock of the chamber. If at any time the bubbling stops in A and the liquid starts to go back the flame should be momentarily removed. The boiling of the melt should not be too violent. When the vacuum is exhausted the stopcock is closed and the apparatus disassembled. The fusion is rolled in the tube, making ready for another determination, and the chamber set aside to be read at the end of three hours. If the melting point of the fusion seems too high, fresh bisulfate should be added before the next determination. If a second determination is not desired, the fusion is poured out while still molten. At the end of three hours the electroscope head is placed on the chamber, and charged for 15 minutes. The negative side of the battery is connected to the case and the positive to the leaf. Before taking a reading the stopcock is quickly opened and closed to bring the chamber to atmospheric pressure. The barometric reading and temperature should be recorded. The rate of discharge is proportional to the pressure and inversely proportional to the absolute temperature. The time of discharge of the leaf from 8 to 4 is taken. From three to ten readings should be made. The discharge is calculated in divisions per second. The natural leak or a blank is subtracted from this. A blank is run with distilled water. This is usually just a little more than the natural leak. This discharge is compared with that of a standard.

Example of a Determination and Calculation.—

0.5 g. of sample sealed Oct. 1, at 5:00 P.M.
Boiled off Oct. 5, at 8:30 P.M.
Time of recovery 3 days, 15½ hours.
Recovery factor for 3 days 15 hours, 0.47926 See table
½ hour 0.00193

log of 0.4812, $\bar{1}.6822$
colog of 0.4812, .3178

A—II. Time of discharge over 40 divisions of the head on chamber II, 92.5 sec.

B—II. Time of discharge over 40 divisions of head B on chamber II, 100 sec.

1.6021 log of 40	$\bar{1}.6330$ log of 0.4295
1.9661 log of 92.5	$\bar{9}.9450$ standardization of instrument
$\bar{1}.6360$ log of 0.4325	.3178 colog recovery factor
Blank .0030	.3010 To change from 0.5 to 1 g.
	2.6567 log factor, grams to pounds
0.4295	3.3010 Conversion to ton
	$\bar{2}.1545$ = 14.3 mg. per ton.

B—II is calculated in the same way. The standardization of this particular instrument was 9.9825. The last four numbers of the above calculation are the same in both cases. The number for the standardization of the instrument is the log of the number of grams of radium necessary to discharge the leaf one division per second. This is obtained by running through the instrument radon from pitchblende, carnotite, or a radium solution the radium content of which is accurately known. In all cases the natural leak or blank must be subtracted.

The instrument is charged 15 minutes before the readings are made in order to allow the active deposit of RaA, RaB and RaC to collect on the wall of the chamber. This also gives the instrument the electric "soak." Successive readings will now check. The leaf system should be charged positively. The readings are taken at the end of three hours after the radon is drawn into the chamber. The activity increases to a maximum at that time. For the first part of the period the increase is very rapid. The maximum is actually reached at the end of four hours, but between three and five hours the curve is practically flat.

A six inch square of asbestos board with a hole in the middle to fit the test tube should be placed on a ring just above the fusion to prevent burning the stopper or melting the paraffin. This is not shown in Fig. 90.

As soon as the readings are made the instruments must be freed from radon by drawing dry air through them, the air being dried by sulfuric acid.

Carbonate Fusion.—About 2 grams of a mixture of sodium and potassium carbonates are placed in a platinum boat about 2 in. long, ½ in. wide and ½ in. deep. Larger boats may be used for low grade samples, Fig. 91, where large amounts are taken for analysis. From 0.05 to 1 gram of the sample should be weighed into the boat. The boat is now filled level full of the fusion mixture. The fusion is made over a flame, or better in an electric furnace at about 1000° C. If the boat is put in the furnace while it is cool, the fusion mixture will dry and melt slowly as the furnace heats up, and thus prevent "boiling over." When thoroughly fused and while still at the highest tem-

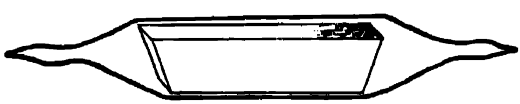


FIG. 91. Boat and Sealed Tube.

perature, suddenly chill the fusion by dipping the boat in water, being careful not to allow water to run into the boat and wet the mixture. The chilling causes the mass to draw away from the boat and in the acid treatment to slip out of the boat. Without this treatment it is very difficult to dissolve the fusion from the corners of the boat. Especially is this true with samples of high silica content. The boat with the fused material is sealed in a glass tube as shown in Fig. 91. The tube should be no longer than necessary. A number of tubes should be prepared in advance by having one end sealed. After

standing one to five or more days the radon surrounding the boat is drawn into an evacuated chamber. The recovery period depends on the amount of radium present and the time the result is demanded. The fourth day is usually about right, giving a little more than 50% recovery of the radon. The chamber may be evacuated by means of an aspirator on the water faucet or

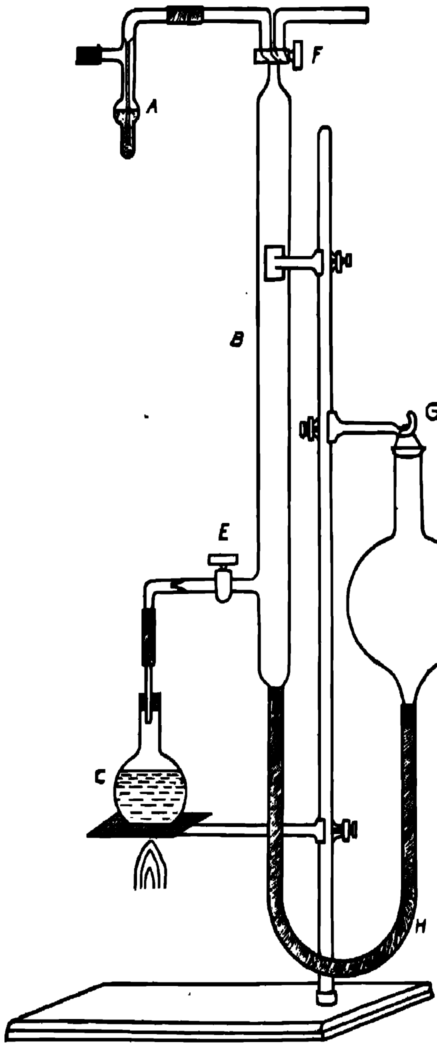


FIG. 92. Apparatus for Radium Determination.

by a pump. To draw radon from the tube to the evacuated chamber a rubber tube is placed on one end of the sealed tube and connected to the chamber with a capillary tube intervening to prevent broken glass from being drawn into the chamber, and a glass stopcock is connected by a rubber tube on the

other end. The tip of the sealed tube is broken with a pair of pliers and the stopcock of the chamber is opened for an instant. The other tip is broken and the glass stopcock opened for an instant. The stopcock of the chamber is opened again and closed after an instant. Air is let through the glass stopcock again. After air is taken through about three times the chamber is ready to receive the radon from the burette. It is necessary to use only a small part of the vacuum to draw the radon from the sealed tube. The tube is broken and the boat is folded in a filter paper in such a manner that the paper will hold the boat in the neck of the flask until the flask is connected with the apparatus shown in Fig. 92. About 2 in. of a stick of sodium hydroxide is placed in leveling bulb *D*. Boiling water is poured on this, and the solution is raised in the burette about three-fourths of its height, having stopcock *E* closed and *F* open. *F* is now closed and the leveling bulb hung on hook *G*. Flask *C* contains 1:1 HNO_3; or if the fusion is very hard to disintegrate, a solution of 3 parts of acid to 2 parts of water may be used. If the chilling is properly done this is usually unnecessary. The boat is shaken into the nitric acid and stopcock *E* opened immediately. A Bunsen burner flame is applied to the flask and the acid brought to boiling. The boiling is continued for 10 to 30 minutes according to the nature of the material. The heating must be regulated so that the solution in the burette is not driven too low. If the flask is heated too strongly the gas may be prevented from escaping through the tube *H* by raising leveling bulb *D*. When the boiling has continued long enough the flame is removed and stopcock *E* closed. The stopcock should be closed just as the solution starts to come back into the flask. Disconnect the burette from the flask. The burette is now connected with the evacuated chamber by means of a microdrying bulb containing sulfuric acid. The stopcock of the chamber is opened very slightly. Then the stopcock of the burette is opened slowly but fully. The stopcock of the chamber is now regulated until the flow of gas is such that the liquid in the burette rises steadily but not too fast. If the air rushes through too fast sulfuric acid will be drawn into the chamber. When the liquid reaches stopcock *F* the stopcock is turned and air let in till the level is about one-fourth down the tube. The air is drawn into the chamber till the liquid again reaches the stopcock. The air is again let in as before. The stopcock is opened into the chamber again and the liquid poured out of the leveling bulb. Air is drawn through the column until the chamber is full. The burette is disconnected, and the chamber set away to be read three hours later. Just before the time to make the reading the electroscope head is placed on the chamber and charged for 15 minutes. The chamber is opened to atmospheric pressure by opening the stopcock only for an instant, Fig. 89. From three to ten readings with stopwatch are taken over forty small divisions, from 80 to 40. The temperature and pressure are noted. If these vary much from the conditions under which the instrument was standardized, a correction of the discharge must be made. The rate of discharge will be proportional to the pressure and inversely proportional to the absolute temperature. The discharge is calculated in divisions per second. The natural leak, or blank, is subtracted from this. Calculations are made as in the bisulfate fusion method.

Gamma Ray Method.—The instrument shown in Fig. 93 is used for this determination. The sample is placed in the holder at such a distance as will cause a reasonable rate of discharge. A standard (containing a known quantity of radium) is then substituted for the sample, and the two rates of discharge compared. The natural leak should be subtracted in each case. The quantities of radium are proportional to the rates of discharge. The difference in radium content of the standard and that of the sample should not be too great.

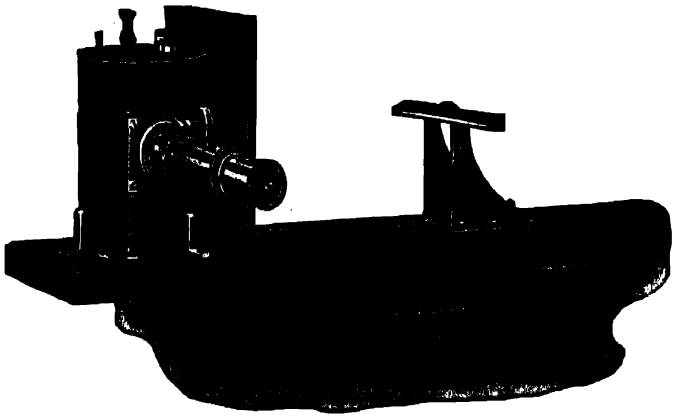


Fig. 93. Apparatus for the Gamma Ray Method.

Method for Solutions.—A measured volume of the solution is placed in a 150-ml. pyrex flask about one-half full. A little barium nitrate should be added to prevent the precipitation of radium sulfate. The solution is boiled to expel all the radon. A special flask with a long neck (about 6 to 8 mm. in diameter) is used. An ordinary flask may be used by inserting a rubber stopper carrying a tube which can be sealed. Or the neck of a pyrex flask can be drawn out and sealed. With the rubber stopper the radon may be lost by leaking. The special flasks are made by the Denver Fire Clay Company. After the radon has recovered for one or more days the flask is connected to the burette by a rubber tube as in Fig. 92. The tip is broken and heat is applied to the flask. On breaking the tip the rubber tube collapses if the flask has not leaked. When the pressure in the tube is about atmospheric the stopcock is opened slightly from time to time until gas begins to bubble into the burette, and then opened wide. The solution is boiled for about ten minutes. The gas is then drawn into an evacuated chamber as described in other methods. The calculation is made in milligrams of radium per liter.

Standardization of Instruments.—One gram of a carnotite ore containing from 10 to 15 mg. of radium per ton is run as directed in the bisulfate fusion. Or 5 ml. of a standard radium solution containing about 10^{-8} gram of radium (in 5 ml. of solution) may be used. These quantities after full recovery will discharge the electroscope with the ordinary aluminum leaf in 30 seconds to 1 minute.

The standardization factor is the quantity of radium necessary to discharge the electroscope one division per second.

Calculation of the Standardization Logarithm.—To the log of the quantity of radium (in grams) add the log of the recovery factor and subtract the log of the corrected discharge.

Example.—5 ml. of a standard (containing 1.573×10^{-8} gram of Ra in 5 ml.) is used. The time of recovery is 3 days and 7 hours. The recovery factor is 0.67775. The time of discharge is 33.6 seconds.

1.6021 log of 40	$\bar{8}$.1967 log of wt. of Ra
1.5263 log of 33.6	$\bar{1}$.8311 log of recovery factor
———	———
.0758	$\bar{8}$.0278
1.191 Antilog of 0.758	.0748 log of 1.188
.0030 Natural leak or blank	———
———	$\bar{9}$.9530 Standardization logarithm.
1.1880 Corrected discharge.	

NOTES.—While the carbonate method as described in Bulletin 104, U. S. Bureau of Mines, is very accurate it has been very largely replaced by the bisulfate method which is also accurate and more convenient. If the fused mass is rolled on the side of the tube, the test tube will never break when the material is melted. Only ordinary precaution is required.

The chief source of radium at present is the Belgian Congo. There is a great quantity of carnotite in western Colorado and eastern Utah. The Congo ore is a great deal higher in uranium and radium content. The Congo ore contains the following minerals: Pitchblende, (primary mineral oxide of uranium) and alteration products; torbernite; Curite (lead uranate); kasolite (silicate uranite). A deposit of pitchblende is found in Canada.

The ratio of radium to that of uranium in pitchblende, carnotite, and other old minerals is 3.4×10^{-7}; or there are 3.4 parts of radium to 10,000,000 of uranium.

For ordinary use radium solutions should contain about one million times as much barium as radium to protect the radium from precipitation by sulfates which may come from glass vessels or other sources.

When readings are made at conditions varying considerably from those at which the instrument was calibrated, a temperature and pressure correction should be made. At higher temperatures and lower pressures the readings are too low because there is less gas to be ionized.

To convert milligrams of radium per ton to percentage of U_3O_8 divide by 2.61.

REFERENCES

Bulletin 70, U. S. Bureau of Mines.

Bulletin 104, U. S. Bureau of Mines.

The Chemical Effects of Alpha Particles and Electrons. S. C. Lind. The Chemical Catalog Co. Inc., 1 Madison Ave., New York.

Radioactive Substances and Their Radiations, E. Rutherford. G. P. Putnam's Sons, New York.

Introduction to the Rarer Elements, Philip E. Browning. John Wiley & Sons. Inc., New York.

Practical Measurements in Radioactivity, W. Makower and H. Geiger. Longmans Green and Company, Fourth Ave. and 30th St., New York.

The Interpretation of Radium and the Structure of the Atom. Frederick Soddy. G. P. Putnam's Sons, New York.

Bulletin 16, Radium, Uranium and Vanadium Deposits of Southern Colorado. Colorado Geological Survey, Boulder, Colo.

Radioactivity, Hevesy and Paneth. Oxford University Press.

Radioactivity and Geology, John Joly. A. Constable and Co., London.

RHENIUM [1]

Re, ***at.wt.*** **186.31;** ***d.*** **21.04;** ***m.p.*** **3167±40° C.;** ***oxides,*** **Re_2O_7, ReO_3, ReO_2, Re_2O_3**

The methods which have been developed for the determination of rhenium are applicable for the most part only to samples containing a relatively high concentration of the element. Although analytical procedures are available for the detection and estimation of small amounts of rhenium, they should be used with caution. When dealing with samples of unknown composition, it is advisable to check the method on similar samples to which known amounts of rhenium have been added.

OCCURRENCE

Rhenium is an exceedingly rare element. Although it has been reported in a number of minerals, its principal occurrence seems to be with molybdenite. The richest native molybdenum disulfide thus far investigated contained 0.002% rhenium. Certain other sulfide minerals have been found to contain lesser amounts. Commercially it is said to be obtained from a molybdenum residue produced during the refining of a continental copper ore.

DETECTION

In the group separations, heptavalent rhenium concentrates in the hydrochloric acid insoluble sulfide fraction. If the presence of rhenium is suspected, the acid concentration should be raised to at least 5% by weight and the passage of hydrogen sulfide continued for one hour. Extraction of the precipitate with sodium sulfide solution will remove the molybdenum, leaving the bulk of the rhenium heptasulfide undissolved. Upon digestion of the residue with 5% NaOH solution and 30% H_2O_2, the rhenium sulfide passes into solution as sodium perrhenate. The hydrated oxides are filtered off, the fil-

[1] Chapter by Loren C. Hurd.

trate concentrated to a small volume, and the presence or absence of rhenium determined microscopically by adding to a drop of solution, solid caesium chloride. Rhenium, if present, will be precipitated as $CsReO_4$ in the form of small highly refracting bi-pyramids isomorphous with $CsClO_4$. A trace of $KMnO_4$ added to the test drop serves to stain the crystals and make them more readily discernible in the field. The method works well with materials containing a minimum of 1% Re.

Identification of rhenium in the extracted sulfide residue may also be done spectrographically. The most persistent lines of rhenium have wave lengths of 3451.28 Å, 3460.47 Å, and 3463.72 Å. Direct spectrographic examination of minerals is to be avoided unless an instrument of very high dispersion is available. The practical coincidence of lines of iron, manganese, and molybdenum with one or more lines of the triplet, makes the identification difficult and questionable.

Flame, bead, and röstrohr reactions have been proposed, but none is wholly satisfactory.

ESTIMATION

The most satisfactory method for the quantitative determination of the element consists of isolating rhenium from the bulk of interfering materials by distilling it from hot concentrated sulfuric acid through which a current of moist HCl is passed. Rhenium heptasulfide is precipitated in the distillate, and this is converted to perrhenate by means of 5% NaOH and 30% H_2O_2. From this solution, nitron perrhenate is precipitated and weighed.

Small amounts of the element may be estimated colorimetrically by adding to an HCl solution of $HReO_4$, $SnCl_2$ and KSCN. The yellow complex developed is extracted with ether, and the rhenium estimated by comparing the intensity of the color with that of standards prepared by treating known amounts of perrhenate solution in a similar manner.

Proposed methods based upon the precipitation of ReO_2, $AgReO_4$, $TlReO_4$, $KReO_4$, or upon the direct weighing of the sulfide, are unsatisfactory.

PREPARATION AND SOLUTION OF SAMPLE

Prolonged acid digestion of rhenium-containing samples should be avoided because of danger of loss by volatilization. If an equivalent amount of fixed base be present, the sample may be safely digested with muriatic acid. The evolution of chlorine does not result in rhenium losses provided the temperature of the solution is held below 100° C. Although most compounds may be dissolved by warming with 5% NaOH and 30% H_2O_2, some few, notably

ReS_2, resist the action of this mixture. Fusion with Na_2O_2 will convert any known compound or metallic rhenium to soluble perrhenate.

SEPARATIONS

Because the general analytical methods for the determination of rhenium have not been rigorously established for all types of mixtures, hard and fast recommendations for the determination of the element in minerals and concentrates cannot be given at this time. The methods described have been used with success upon relatively simple mixtures and upon concentrates of known composition. When adapting them to complex samples, it is strongly recommended that controls to which known amounts of rhenium have been added be carried through the entire composite procedure.

Separation from Molybdenum.—One of the most efficient and satisfactory methods yet devised for separating rhenium and molybdenum consists of distilling the rhenium out of a sulfuric acid solution through which a current of hydrogen chloride is passed. The apparatus consists of three connected units, viz.: A hydrogen chloride generator, a 500-ml. round-bottom flask provided with an inlet leading to the bottom of the flask, and an exit arranged to carry off hydrochloric acid vapors, and a side arm distilling flask. The distilling flask is provided with a ground glass stopper through which an inlet tube reaching to the bottom of the flask is sealed. The side arm is bent to allow for the connection of a vertical water-cooled condenser. The open receiver is an Erlenmeyer flask packed in an ice bath. It has been found convenient to maintain a constant flow through the system by means of a slow current of carbon dioxide passed through the hydrogen chloride generator.

The sample, which may consist of the sodium hydroxide-hydrogen peroxide solution of a sulfide residue or a solid sample, is placed in the ground glass stoppered distilling flask and acidified with 150 ml. of 80% H_2SO_4 and 10 ml. H_3PO_4. 300 ml. of HCl (sp.gr. 1.2) is placed in the round-bottom flask, and the air in the system displaced with hydrogen chloride and carbon dioxide. The temperature of the sulfuric acid is slowly raised to about 160° C. The solution of hydrochloric acid is then slowly heated and about 200 ml. of the hydrochloric acid distilled over during the course of an hour. The distillate contains all of the rhenium.

If the original sample was known to contain over 1.0 gm. of molybdenum, it is well to repeat the distillation in order to free the concentrate from the trace of molybdenum which sometimes accompanies the rhenium. The distillate is then treated with hydrogen sulfide in the manner described under sulfide-nitron determination.

8 Hydroxyquinoline Separation.—A solution of not over 150 ml. containing alkali molybdate and perrhenate is brought to neutrality with either sodium hydroxide or sulfuric acid, rendered slightly acid with 5 ml. NH_2SO_4, and buffered with 5 ml. 2 N sodium acetate. A 5% solution of 8-hydroxy quinoline is added slowly and with constant stirring, until precipitation is complete. The precipitated oxine molybdate is filtered off, washed, and rhenium determined in the filtrate. It is advisable to first precipitate the rhenium as the sulfide and determine as nitron perrhenate, rather than attempt a direct precipitation with nitron.

SULFIDE-NITRON DETERMINATION

The solution of heptavalent rhenium containing between 5% and 10% hydrogen chloride (weight basis) is heated to 70° C. and a slow current of hydrogen sulfide bubbled in for at least an hour. The sulfide precipitate is filtered off on an asbestos pad, washed thoroughly with hydrogen sulfide saturated water, and the filter pad and its contents transferred to a small beaker. The Re_2S_7 is warmed with a few ml. of 5% NaOH and 30% H_2O_2 until all of the black particles have dissolved and no trace of yellow color remains in the solution. The asbestos is filtered off on a small paper and thoroughly washed with small portions of hot water. If the volume of the filtrate exceeds 50 ml. it is evaporated and then rendered slightly acid with dilute H_2SO_4. The solution is boiled to coagulate the small amount of silica generally thrown down, filtered, and to the hot filtrate 10 ml. 5% nitron acetate added. The solution is stirred frequently during subsequent cooling. When it reaches room temperature, the beaker is placed in an ice bath, where it is further cooled for an hour. The precipitated nitron perrhenate is filtered off on a Gooch crucible, washed with an ice cold saturated nitron perrhenate solution containing 0.1% nitron acetate, and finally with 1–2 ml. ice cold distilled water. The precipitate is dried at 105° C. for an hour, and weighed. The weight of the precipitate, multiplied by 0.3306, gives the weight of rhenium in the original sample.

COLORIMETRIC DETERMINATION

The solution, containing between 10γ and 500γ of rhenium, and free from molybdenum and platinum, is placed in a separatory funnel and sufficient HCl added to bring the acid concentration to 2% (weight basis). The solution is cooled to room temperature, and 2% $SnCl_2$ added in sufficient quantity to bring the concentration to 0.2%. This is followed immediately with enough 10% KSCN to give a concentration of 0.4%. After standing for seven minutes, the yellow rhenium oxythiocyanate is extracted with three successive 25-ml. portions of ether which has been previously shaken with $SnCl_2$ and KSCN, and the combined extracts immediately compared with standards prepared by treating known amounts of potassium perrhenate in the manner described. It is essential that both standards and sample be treated exactly the same, and that the comparisons be made promptly.

SCANDIUM

Sc, *At.wt.* 45.10; *Oxide:* Sc_2O_3 [1]

OCCURRENCE

Scandium is very widely distributed in minute quantities in almost all rocks, but it is found in appreciable quantity only in very few minerals. Micas, cassiterite and wolframite from some localities, euxenite and keilhauite contain a few tenths per cent of scandia; wiikite contains a little over one per cent and thortveitite, the only mineral of which scandia is an essential constituent, over thirty per cent.

DETECTION

In qualitative analysis, scandia is found in the ammonia precipitate. This is dissolved in hydrochloric acid, the solution neutralized and boiled with sodium thiosulfate, and the precipitate dissolved in hydrochloric acid. After filtration from sulfur, scandium and thorium oxalates are precipitated by addition of oxalic acid. The washed precipitate is digested with fuming nitric acid; the solution is evaporated to dryness, the residue dissolved in a little water, the solution poured into a twenty per cent solution of ammonium tartrate and the mixture boiled with ammonia; the gradual separation of a crystalline precipitate indicates the presence of scandium.

In the examination of mixtures of the rare earths, which often contain scandia, the mixed oxides obtained by ignition of the oxalates (see Rare Earths Chapter) are dissolved in hydrochloric acid, and the solution boiled with sodium silicofluoride: a heavy gelatinous precipitate of scandium fluoride is obtained, free from all but traces of rare earths.

Minute quantities of scandia are readily detected by examination of the spark spectrum. The scandium must first be concentrated together with any rare earths by precipitation with oxalic acid. The precipitate is ignited to oxides, which are dissolved in hydrochloric acid; the filtrate from the oxalates should be examined also for scandia. The most intense scandium lines lie between 3500 and 3700 Å; they are 3572.72, 3613.98, 3630.90, 3642.96.

[1] Chapter by W. R. Schoeller, Ph.D., and A. R. Powell, Metallurgical Chemists, London, England.

PREPARATION OF THE SOLUTION

Minerals containing rare earths are decomposed by treatment with hydrochloric or sulfuric acids or by fusion with sodium pyrosulfate. Euxenite, and similar minerals containing titanium, tantalum, and columbium, may be decomposed by attack of the moistened, finely powdered sample with forty per cent hydrofluoric acid, and, after the violent action has subsided, evaporation to dryness on the water bath. The residue is extracted with boiling water, the insoluble material collected on a rubber funnel, and dissolved by heating with concentrated sulfuric acid. Wolfram, which sometimes contains scandia, is decomposed by digestion of the slimed mineral with aqua regia.

ESTIMATION

The solution obtained by any of the above methods is saturated with hydrogen sulfide to remove heavy metals, and the filtrate boiled to expel the gas and oxidized with nitric acid. The hot solution is treated with a slight excess of ammonia, the precipitate collected, well washed with two per cent ammonium nitrate solution, and dissolved in the minimum of 1 : 1 nitric acid; the solution (50 to 60 ml.) is treated hot with 20 ml. of a saturated solution of oxalic acid added slowly during agitation. After standing overnight the precipitate is collected, washed with a dilute solution of oxalic acid, rinsed back, and digested with fuming nitric acid till completely dissolved. The nitrates are converted into chlorides by two evaporations to dryness with hydrochloric acid. The residue is dissolved in 200 ml. of hot water and the solution boiled with 10 g. of sodium thiosulfate for one hour. The precipitate is filtered off, washed, and dissolved in hydrochloric acid, the filtered solution evaporated to dryness, the residue dissolved in water, and the thiosulfate precipitation repeated with 5 g. of the reagent in a bulk of 150 ml. The second precipitate is treated as the first, and the filtered solution neutralized with ammonia. One drop of 1 : 1 hydrochloric acid is added, and the solution (50 ml.) allowed to drop slowly into 50 ml. of a boiling twenty per cent solution of ammonium tartrate. Boiling is continued with the occasional addition of a few ml. of ammonia, for forty minutes. After standing until cold, the solution is filtered; the precipitate is washed with cold five per cent ammonium tartrate solution, and ignited wet in a platinum crucible. After ignition at high temperature, the residue is weighed as Sc_2O_3.

In the case of wolfram, the solution obtained by digestion of the mineral with aqua regia is boiled with 5 g. of sodium silicofluoride for an hour. The precipitate of scandium fluoride is collected, washed with hot water, and heated in a platinum dish with concentrated sulfuric acid until copious fumes are evolved. After cooling, the residue is dissolved in water, and the scandium precipitated with ammonium tartrate as described above.

SELENIUM AND TELLURIUM[1]

Se, *at.wt.* 78.96; *sp.gr.* $\left\{\begin{array}{l}\textit{Cryst.}\ 4.82;\\ \textit{Amorp.}\ 4.26;\end{array}\right.$ *m.p.* 217° C. $\}$ *b.p.* 690° C.; *oxides*, SeO_2, SeO,
Te *at.wt.* 127.61; *sp.gr.* 6.24; *m.p.* 452; *b.p.* 1390° C.; *oxides*, TeO_2, TeO

Selenium and tellurium are closely associated with each other and with sulfur, which they closely resemble. Selenium was discovered by Berzelius (1817) in the flue dust of the pyrites burners, since it occurs in iron pyrites. It is found as an impurity in sulfuric and hydrochloric acid. As selenide it occurs combined with bismuth, copper, lead, mercury, iron and silver. The commercial source is from the mud in the vats of copper refining.

Tellurium is the least abundant of the sulfur group. It is found in nature combined as telluoride of gold, bismuth, copper, lead, mercury, nickel, iron and silver. The sludge from copper refining is a commercial source. Commercial uses remain to be developed.

Ores—Selenium.—In copper and iron pyrites; meteoric iron. In the rare minerals clausthalite, PbSe; lehrbachite, PbSe·HgSe; onofrith, HgSe·4HgS; eucairite, CuSe·Ag_2Se; crookesite, (CuTlAg)Se.[2]

Tellurium.—Occurs in tellurides and arsenical iron pyrites. Frequently associated with gold, silver, lead, bismuth and iron. In the minerals—altaite, PbTe; calaverite, $AuTe_2$; coloradolite, HgTe; nagyagite, $(AuPb)_2(TeSSb)_3$; petzite, Ag_3AuTe_2; sylvanite, $AuAgTe_4$; telluride, TeO_2 (tellurium ochre); tetradymite, Bi_2Te_3.[2]

DETECTION

Selenium and tellurium are commonly detected by precipitation with sulfur dioxide in hydrochloric acid solution. A selenium solution containing strong hydrochloric acid in the cold gives with either sulfur dioxide gas or the aqueous solution the amorphous red variety which, on warming, goes to the gray crystalline form. Tellurium solutions in presence of dilute hydrochloric acid with sulfur dioxide yield black elementary tellurium.

[1] The crystalline variety of selenium has the property of being a good conductor of electricity when exposed to light and a poor conductor in the dark. Advantage is taken of this in measuring the intensity of light in the stars and in certain electrical devices for the automatic control of lighting of buoys. It is used for coloring glass red and for counteracting the green color in glass. Its similarity to sulfur suggests its use for rubber manufacture in place of sulfur and as a fungicide.

[2] Thorpe, "Dictionary of Applied Chemistry."

Hydrogen sulfide gives with selenious acid solutions a precipitate which is at first lemon yellow but on standing changes over to red, due to the dissociation of yellow sulfide of selenium into sulfur and amorphous red selenium. Tellurous solutions with hydrogen sulfide give at first a red brown precipitate which rapidly darkens due to dissociation into elementary tellurium and sulfur. Both of the sulfides are soluble in alkaline sulfide solutions.

Stannous chloride, ferrous sulfate, hydroxylamine hydrochloride, hydrazine hydrochloride, phosphorous acid, or hypophosphorous acid added in the cold to selenious solutions give red elementary selenium, which goes over to the black variety on warming. Potassium iodide added in excess to a hydrochloric acid solution of either a selenite or selenate gives, in the cold, red selenium together with iodine. On warming the iodine distils and the red selenium goes over into the gray form.

A tellurium solution yields black elementary tellurium when treated with stannous chloride, hypophosphorous acid, hydrazine hydrochloride or with metals like zinc, aluminum, and magnesium.

Neutral selenious solutions with barium chloride give a precipitate of barium selenite which is soluble in hydrochloric acid. Neutral selenates with barium chloride yield insoluble barium selenate, which, like all selenates, is decomposed with the evolution of chlorine and subsequent reduction to the selenite which dissolves in the hydrochloric acid.

The few soluble alkaline tellurites give with barium chloride a white precipitate of barium tellurite which is soluble in hydrochloric acid. Barium tellurate is precipitated when a tellurate solution is treated with barium chloride. It is decomposed by hydrochloric acid, yielding chlorine and forming barium tellurite which dissolves in hydrochloric acid.

Sulfuric Acid Test.—Selenium or a selenide with concentrated sulfuric, gently warmed, or fuming sulfuric acid, in the cold, gives a green color, the intensity of which varies from a light green to an almost opaque greenish black, depending on the amount of selenium present. When the green solution is added to water, red elementary selenium is precipitated. This red selenium when boiled in the diluted acid changes into the gray crystalline form. The green color in the concentrated sulfuric acid is destroyed by warming the solution a few minutes. This test is not applicable to an oxidized selenium compound.

Tellurium or a telluride, but not oxidized tellurium compounds, gives in the cold with fuming sulfuric acid or with warm concentrated sulfuric acid a red color, the intensity of which depends on the amount of tellurium present. When the red solution is poured into water, black elementary tellurium is precipitated. When the red solution is warmed, sulfur dioxide is evolved, the red color disappears and if much tellurium is present, white crystals of the basic sulfate of tellurium separate.

The sulfuric acid test is frequently of no value when both of the elements are present, since the red of the tellurium may obscure the green of the selenium.

QUALITATIVE DETECTION OF SELENIUM AND TELLURIUM IN COMPLEX MIXTURES

First Method.—The substance is treated with aqua regia or with a mixture of hydrochloric acid and potassium chlorate, and the free chlorine is expelled by warming at a temperature below boiling in order to avoid loss of volatile chlorides. The solution is then diluted and filtered to remove insoluble matter. Should tellurous acid precipitate on diluting with water, it can be redissolved by hydrochloric acid. The acid solution is treated with sulfur dioxide gas, or sodium acid sulfite. The formation of a precipitate indicates the possible presence of selenium, tellurium, or gold. (1) If the precipitate is allowed to settle, the liquid poured off, and the precipitate warmed with strong nitric acid, selenium and tellurium will dissolve leaving the gold insoluble. The nitric acid solution can be evaporated with hydrochloric acid to destroy the nitric acid and then treated in concentrated hydrochloric acid solution with sulfur dioxide gas. If selenium is present, it will appear as a red precipitate which on warming goes to the gray crystalline. The selenium precipitate can be filtered off through an asbestos filter and the solution when diluted with water and more sulfur dioxide added gives a black precipitate of elementary tellurium. (2) The sulfur dioxide precipitate containing possible selenium, tellurium, and gold can after washing be treated directly with hot concentrated sulfuric acid in order to get if possible the characteristic selenium or tellurium colors.

Second Method.—Crude selenium or tellurium-bearing material from any source whether oxidized or non-oxidized can be fused with five to six times its weight of potassium cyanide. Tellurium forms potassium telluride, selenium forms selenocyanate, and sulfur, which is invariably present, gives sulfocyanate. Extraction of the fused mass with water gives a purple solution if tellurium is present, the selenocyanate and sulfocyanate being colorless. The heavy metals remain insoluble, and can be removed by filtration. When a current of air is bubbled through the solution, the purple color is discharged and black elementary tellurium is precipitated. This tellurium can be filtered off and verified by the sulfuric acid test.

The selenocyanate and sulfocyanate from the air oxidation of the potassium telluride solution can be treated *under a good hood* with hydrochloric acid, when hydrocyanic acid is set free and red selenium is precipitated. The selenium can be confirmed by conversion to the black variety by heat or the sulfuric acid test can be applied.

ESTIMATION

In the determination of selenium and tellurium where special precautions are not taken in regards to these elements, loss will occur due to volatilization during the acid attack of the material with concentrated HCl and application of heat. Practically no loss occurs with dilute HCl (less than 20%, sp.gr. 1.1 or less) provided the temperature is kept under 100° C. Loss is prevented by digestion with HCl using a reflux condenser. If considerable iron, or aluminum or calcium is present selenium and tellurium will be carried down by the ammonia precipitate and, if not accounted for, will lead to error in the iron and aluminum determinations.

PREPARATION AND SOLUTION OF THE SAMPLE

Decompositions may be affected by fusions with oxidizing fluxes such as sodium carbonate and nitrate, sodium peroxide etc., nickel crucibles being used, since platinum would be attacked. In the HCl action on the fused mass precautions should be taken to avoid loss by volatilization, using dilute HCl and keeping the temperature below the boiling point. Attack by means of oxidizing acids is often advisable, aqua regia or HCl with $KClO_3$ often being preferred. After expulsion of chlorine with additional HCl evaporations are conducted on the steam bath.

SEPARATIONS

Selenium and tellurium are separated from a large number of substances by first reduction to the quadrivalent form and then reducing further to the elemental form by certain reducing agents in HCl solution. Sulfur dioxide and hydrochloric acid are generally preferred for this reaction. Considerable care should be exercized to keep the temperature below the boiling point to prevent loss of the elements by volatilization. The elements are generally precipitated together and later separated. Gold, platinum, and small amounts of antimony, bismuth and copper will precipitate with selenium and tellurium. Details of the procedures follow.

In the precipitation of selenium the element is best obtained by addition of a water saturated solution of sulfur dioxide rather than by bubbling SO_2 through the solution.

Separations of selenium and tellurium from other elements can be readily accomplished. Heating of the selenide and telluride combinations or mixtures in chlorine gas affords a separation from the metals whose chlorides are non-volatile.

Heating of selenites or tellurites in a current of hydrochloric acid gas forms volatile $SeO_2 \cdot 2HCl$ or $TeO_2 \cdot 2HCl$, while the selenates or tellurates give chlorine in addition. This treatment with hydrochloric acid gas, when applied to the oxidized selenium and tellurium compounds, is an excellent means of separation from the metals whose chlorides are non-volatile.

Both of these elements can be separated from most of the more common elements by the general principle of reducing their compounds and precipitating them in elementary form by means of sulfur dioxide, hydrazine or hydroxylamine. Gold is precipitated at the same time but can be separated by treating the well-washed precipitate with nitric acid, sp.gr. 1.25, which will dissolve the selenium and tellurium but not the gold. The nitric acid solution can then be carefully evaporated with hydrochloric acid to destroy the nitric, and convert to chloride solution.

SEPARATIONS OF SELENIUM AND TELLURIUM

Keller's method is to separate the selenium and tellurium from each other by making use of the principle that selenium is completely precipitated by sulfur dioxide from concentrated hydrochloric acid solution while tellurium is not.

Procedure.—The two elements are separated from the other elements by sulfur dioxide in dilute hydrochloric acid solution. The washed precipitate is dissolved in nitric acid and the solution evaporated to dryness on the water bath. The residue is dissolved in 200 ml. of hydrochloric acid, sp.gr. 1.175, and the solution warmed to expel all free nitric acid. The solution is then saturated with sulfur dioxide gas at 15–22° C. The precipitated selenium is allowed to settle, washed first by decantation with cold hydrochloric acid, sp.gr. 1.175, then with cold water to displace the acid and finally treated in the beaker with boiling water which transforms the red selenium into the black granular variety. The selenium is brought on a Gooch crucible washed with alcohol and dried at 105° C. The tellurium is precipitated in the filtrate by diluting with water, adding more sulfur dioxide and hydrazine hydrochloride as in the gravimetric method for tellurium. The tellurium is finally washed with water, then alcohol, dried at 105° C. and weighed.

NOTE.—Loss of selenium occurs with prolonged slow bubbling of SO_2 gas into the solution. It is preferable to add the SO_2 at one time by means of a saturated water solution of the gas.

THE DISTILLATION METHOD OF SEPARATING SELENIUM FROM TELLURIUM [3]

This method is based on the volatility of selenium chloride from sulfuric acid solution when treated with hydrochloric acid gas, while tellurium chloride is nonvolatile under the same conditions. Scott's distillation method offers distinct advantages over other separations of selenium from the various metals in that none of the common elements naturally associated with selenium form volatile chlorides under the conditions of the experiment. Further, the

[3] Victor Lenher and D. P. Smith, J. Ind. Eng. Chem., 16, 837 (1924).

selenium when distilled is collected in hydrochloric acid solution, from which it can be readily precipitated.

Apparatus and Procedure.—The apparatus found to be the simplest and to give the most accurate results is shown in the figure. It consists of a 150-ml. Pyrex distilling flask, *A*, with a glass tube, *B*, sealed in the top of the neck and extending to within 7 mm. of the bottom of the flask. The condenser tube, *C*, is sealed directly in the neck of the flask as close to the top as possible. The receiver consists of three Drexel wash bottles, D_1, D_2, D_3, sealed together and connected to the end of the condenser by means of a ground-glass joint. These bottles at the beginning of the determination are half full of distilled water. The sample of selenium and tellurium-containing material is introduced into the flask through the tube *B*. The sample is washed down with enough sulfuric acid, specific gravity 1.84, to bring the volume of the solution to about 60 ml. Hydrochloric acid gas is now introduced from the generator *E* through the tube *B*. The generator consists of a 3-liter flask into which, by means of a dropping funnel, concentrated sulfuric acid is introduced into concentrated

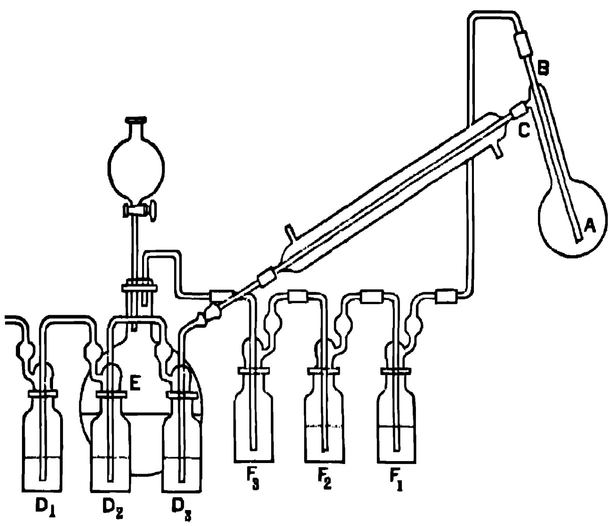


FIG. 94. Apparatus for Separating Selenium and Tellurium.

hydrochloric acid. F_1 and F_2 are wash bottles containing concentrated sulfuric acid; F_3 is an empty bottle. The flask *A* is now heated by means of a Bunsen burner. The temperature is sufficiently controlled by observation of the sulfuric acid in the distilling flask. The acid is at the correct temperature, 300° to 330° C., when slight fumes of sulfur trioxide are evolved. The flame of the burner is then reduced a little and the distillation continued until all the selenium has distilled over, which ordinarily requires 3 to 4 hours. The distilled selenium is collected in the receiver bottles and is determined after transferring to a beaker and adding SO_2 reagent to the solution at a temperature of 15° to 22° C. Red elementary selenium is precipitated from this strong hydrochloric acid solution. The precipitate is allowed to settle and is washed by decantation with cold water several times. Hot water is then poured on

the precipitate in the beaker, when the red selenium is transformed into the gray, granular variety, which is brought on a Gooch crucible, washed with alcohol, dried at 105° C., and weighed. The tellurium solution remaining in the distilling flask is poured into water and diluted with sufficient water so that the content of free sulfuric acid is less than 25%. Enough hydrochloric acid is added to make the solution 7% acid. The tellurium is precipitated from this solution by means of sulfur dioxide and hydrazine hydrochloride according to the method of Lenher and Homberger.[4]

The most important details of the apparatus are in the construction of the flask *A*. It is necessary that the tube *B* should join the top of the flask as close to the exit of the condenser tube *C* as possible. Should any great distance separate these junctions, selenium tetrachloride will condense in the solid form and will not be driven over into the condenser.

The sulfur trioxide fumes must rise to the top of the flask so that the hydrochloric acid gas may sweep all the selenium chloride vapors out of the flask into the condenser and receiver.

Results.—The method is accurate for either high or low amounts of selenium or tellurium. Good results are obtained with varying ratios of selenium and tellurium.

The selenium and tellurium-containing material can be introduced into the flask in various combinations, but obviously hydrochloric or sulfuric acid solutions are the most desirable.

Determination of Selenium.—The solution in the beaker is treated with water saturated with SO_2, then heated to boiling and the precipitated selenium allowed to settle several hours, or overnight. The precipitate is filtered into a weighed Gooch crucible, then washed with hot water and finally with alcohol. The residue is dried for an hour at 100° C. and weighed.

$$\frac{\text{Weight of Se} \times 100}{0.5} = \%\ \text{Se}.$$

Determination of Tellurium.—The residue in the distilling flask is transferred to a 600-ml. beaker containing 150 ml. of cold water. Ten ml. of 3% $Fe(NO_3)_3$ solution is added, and made ammoniacal, and then heated to boiling; the precipitate filtered off on a large filter and washed with hot water. The precipitate is dissolved in hot dilute HCl and the solution nearly neutralized with NH_4OH. The slightly acid solution is saturated with H_2S, the precipitated tellurium filtered off on an S. and S. No. 589, 12½ cm. filter, and washed with H_2S water.

The precipitate is dissolved off the paper into a small beaker with a mixture of equal parts of HCl and bromine-potassium bromide solution.[5] The paper is washed with water keeping the volume of the solution as small as possible. The filtrate should contain 20% HCl.

Tellurium is precipitated by saturating the solution with SO_2. The precipitate, after heating to boiling, is allowed to settle for several hours and filtered

[4] Lenher and Homberger, J. Am. Chem. Soc., 30, 387, 1908.
[5] Thorpe, "Dictionary of Applied Chemistry." Longmans, Green & Co.

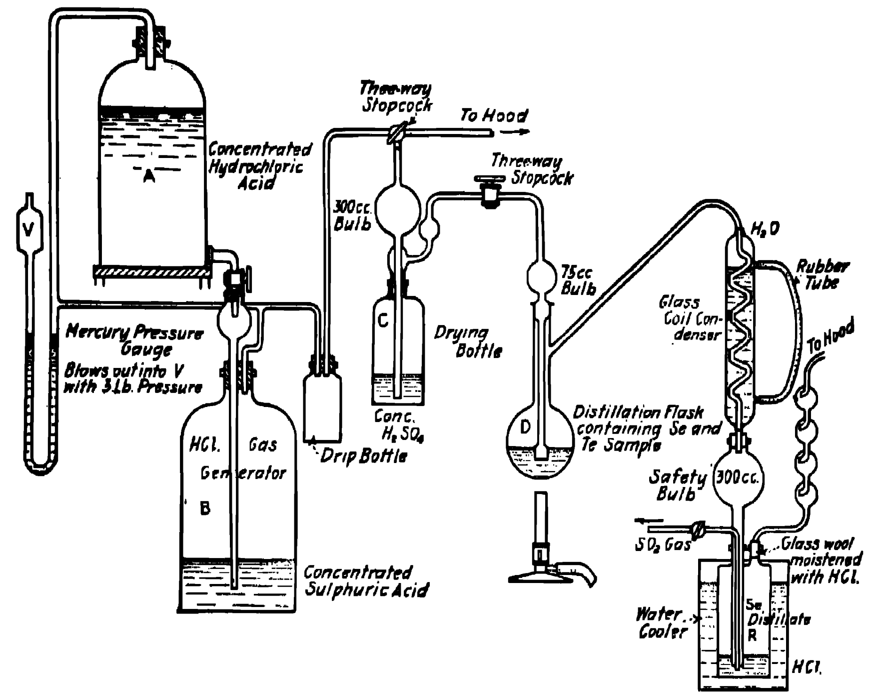


FIG. 95. Apparatus for Determining Selenium and Tellurium.

Fig. 95 shows a convenient apparatus for routine determinations of selenium and tellurium in alloys. Hydrochloric acid gas is generated by allowing strong hydrochloric acid to flow into concentrated sulfuric acid (see *A* and *B* in drawing Fig. 95). The gas is dried by passing it through strong sulfuric acid (*C* in figure). A mercury pressure gauge, arranged to allow gas to blow out at a pressure of 3 or 4 pounds, prevents accidents occurring due to stoppage in the system.

onto a weighed Gooch. It is washed with hot water and then with alcohol and dried for an hour at 100° C., cooled in a desiccator and weighed.

$$\frac{\text{Weight of Te} \times 100}{0.5} = \%\ \text{Te}.$$

THE SEPARATION OF SELENIUM AND TELLURIUM BY SULFUR DIOXIDE IN HYDROCHLORIC ACID SOLUTION [6]

The procedure recommended is as follows. The oxides of the two elements, which should not contain more than 0.25 g. of either selenium or tellurium, are dissolved in 100 ml. of cold concentrated hydrochloric acid; 50 ml. of concentrated hydrochloric acid saturated at ordinary temperature with sulfur dioxide (this is sufficient to prevent the formation of the monochloride) is added during constant stirring. When concentrated hydrochloric acid is used with a large excess of sulfur dioxide, selenium monochloride is not formed in the cold. The solution is then allowed to stand until the red selenium subsides, is filtered through an asbestos filter into a filtering flask, and the precipitate thoroughly

[6] Victor Lenher and C. H. Kao, J. Am. Chem. Soc., 47, 769 (1925).

washed with cold, concentrated hydrochloric acid, then with cold water until it gives no test for chlorine, and finally with alcohol to displace the water, and ether to displace the alcohol. This is necessary, as water must not be allowed to remain in the red selenium, or later it cannot be removed. The red selenium is dried for three to four hours at 30–40° C. to remove the last traces of ether, after which it is heated to 120–130° C. for one to two hours to render the selenium perfectly dry. Whenever any moisture is allowed to remain in the red selenium when it is transformed to the black variety, high results due to oxidation inevitably result. The filtrate from the selenium is then concentrated to 50 ml. to remove the excess of acid. This is done on the steam-bath below 100° C.; otherwise the tellurium may be boiled off as chloride in this strongly acid solution. The tellurium is then precipitated by the Lenher-Homberger method; 15 ml. of a saturated solution of sulfur dioxide is added, then 10 ml. of a 15% solution of hydrazine hydrochloride followed by an additional 25 ml. of a saturated solution of sulfur dioxide, and the solution is boiled. Complete precipitation of the tellurium is almost instantaneous.

The precipitate is washed with hot water on a Gooch filter until all of the chlorine is removed, after which the water is displaced by alcohol as quickly as possible to prevent oxidation of the tellurium, and the crucible and contents are dried at 105° C. Under these conditions of precipitation, tellurium does not oxidize, and the analysis gives more accurate results than by any other method.

Note on Other Methods of Separations.[7]—It is possible to separate selenium and tellurium in hydrochloric, tartaric or citric acid solution by means of hydroxylamine hydrochloride. The sulfate of hydroxylamine proves to be less satisfactory. The procedure of separation is very simple and is susceptible of wide variations in the details of technique.

Both hydrazine hydrochloride and the sulfate tend to cause precipitation of tellurium with the selenium; this can be avoided in the method of Pellini by proper control of temperature.

By use of oxalic acid, it is possible by means of hydroxylamine hydrochloride to separate selenium from tellurium, but the technique is so highly complicated by minor factors that it is not as satisfactory as the tartaric or citric acid methods.

QUANTITATIVE METHODS FOR SELENIUM

Selenium is most commonly precipitated as element by either sulfur dioxide, hydroxylamine or hydrazine. This reduction to element at the same time separates the selenium from most of the elements except tellurium and gold. When hydroxylamine hydrochloride or hydrazine hydrochloride is the precipitating agent, the material is usually most conveniently brought into hydrochloric acid solution and converted if necessary into the selenious state. From this selenious solution, which may be acid, neutral or ammoniacal, these

[7] Victor Lenher and C. H. Kao, J. Am. Chem. Soc., 47, 245, 1925.

reducing agents on boiling precipitate elementary selenium which can be brought on a Gooch crucible, washed with hot water, dried at 105° C., and weighed.

SULFUR DIOXIDE METHOD

The addition of sulfur dioxide to a solution of selenious acid or a selenite which is strongly acid with hydrochloric acid is one of the oldest and best methods of precipitating elementary selenium. A selenate or selenic acid must first be reduced to a selenious acid by warming with hydrochloric acid, after which sulfur dioxide can be introduced by addition of a saturated solution.

It is sometimes convenient to produce the sulfur dioxide by the addition of sodium acid sulfite or of sodium sulfite. This procedure is satisfactory but should be accompanied by a blank test on the sulfite with hydrochloric acid since the sulfites, on standing, not uncommonly give a precipitate of sulfur on acidification.

The best procedure in the precipitation of selenium by sulfur dioxide is to add a saturated solution of SO_2 to the selenious solution which is strongly acid with hydrochloric acid. The solution should smell strongly of SO_2. The beaker is removed and allowed to stand for a half hour, in order that the selenium may settle. The supernatant liquor is decanted through a previously weighed Gooch crucible, and the selenium washed first by decantation with concentrated hydrochloric acid, after which one treatment with cold water is used to wash the precipitate in the beaker. After again decanting, hot water is poured into the beaker containing the precipitate when the flocculent red selenium turns black and granular. It is then filtered, washed with hot water, followed by alcohol and dried at 105° C. to constant weight.

If the temperature in the solution during the precipitation of the selenium rises above 22° C., the selenium agglomerates and occludes impurities which cannot be washed out. If the temperature is below 15° C., the precipitation is either incomplete or very much delayed.

Evaporation of selenious acid should be made on the water bath rather than at a higher temperature since there is an appreciable loss of selenium dioxide when heated above 100° C. In the reduction of selenates or selenic acid to the selenious condition by means of hydrochloric acid, the temperature must never exceed that of the steam bath or considerable selenium may be lost.

POTASSIUM IODIDE METHOD

Potassium iodide added to a selenous solution containing free hydrochloric acid gives a precipitate of elementary selenium, iodine being liberated simultaneously.

$$SeO_2+4HI=Se+2H_2O+2I_2.$$

With samples containing less than 0.1 gram selenium satisfactory results are obtained but with larger amounts iodine is likely to be occluded.

Procedure.—The sample containing selenious acid or a selenite in a dilution of 400 ml. is acidified with hydrochloric acid, 3–4 grams of potassium iodide are added and the iodine liberated is boiled off. The selenium is brought on

a Gooch crucible washed with hot water, dried and weighed. Gooch and Pierce [8] suggest the use of sodium arsenite and iodine solutions in carrying out the method volumetrically.

The thiosulfate method of Norris and Fay [9] consists in treating a hydrochloric acid solution of selenious acid with a measured excess of standard sodium thiosulfate solution and then titrating the excess of thiosulfate with an iodine solution.

$$H_2SeO_3+4Na_2S_2O_3+4HCl=4NaCl+Na_2S_4SeO_6+Na_2S_4O_6+3H_2O.$$

Selenates or **selenic acid** can be analyzed by boiling with hydrochloric acid when chlorine is evolved which can be collected and titrated.

QUANTITATIVE METHODS FOR TELLURIUM

Tellurium can be determined gravimetrically and separated from most of the elements except selenium and gold by a number of reducing agents. The oldest method, that of Berzelius, is the use of sulfur dioxide in slightly acid solution. Black elementary tellurium is precipitated but complete precipitation is much delayed even when the solution is warm. The hydrochloric acid solution of the tellurium should always be allowed to stand twenty-four hours. The tellurium is then conveniently brought on a Gooch crucible and the filtrate further digested after the addition of more sulfur dioxide. Very frequently more tellurium settles out on standing twenty-four hours longer. After all of the tellurium is collected on a Gooch crucible, it is washed and dried at 105° C. as quickly as possible in order to avoid the slight superficial oxidation which always takes place with tellurium which has been precipitated in this manner.

Hydrazine hydrochloride used as a reducing agent for the precipitation of elementary tellurium gives fairly good results but complete precipitation as with sulfur dioxide is somewhat delayed.

The use of sulfur dioxide and hydrazine hydrochloride together is the most accurate as well as the most rapid method for the determination and is applicable to both tellurites and tellurates, as well as to the free acids.

HYDRAZINE HYDROCHLORIDE–SULFUR DIOXIDE METHOD

The tellurium, either as a derivative of the dioxide or as a tellurate, should be present in a solution which has an acidity of approximately ten per cent

[8] Am. J. Sci. (4), I, 31 (1896).
[9] Am. Chem. J., 23, 119 (1900).

free hydrochloric acid, and it is preferable that the solution be concentrated, for otherwise the precipitate will be so finely divided that it will be difficult to wash. The solution is heated to boiling, 15 ml. of a saturated solution of sulfur dioxide is added, then 10 ml. of a fifteen per cent solution of hydrazine [10] hydrochloride followed by 25 ml. of sulfur dioxide solution. The boiling is continued until the precipitate settles in such a way that it can be easily washed, which should not take more than five minutes. The precipitated tellurium is brought on a previously weighed Gooch crucible, washed with hot water until all of the chlorides are removed, after which the water is displaced by alcohol, and the crucible and contents dried at 105° C.

Tellurates or telluric acid can be analyzed by boiling with hydrochloric acid when chlorine is given off.

$$H_2TeO_4 + 2HCl = H_2TeO_3 + Cl_2.$$

The chlorine evolved may be passed into potassium iodide solution and the liberated iodine titrated by sodium thiosulfate or an arsenite solution.

PRECIPITATION AS TELLURIUM DIOXIDE

Browning and Flint [11] utilize the insolubility of tellurium dioxide as a means of separation from the readily soluble selenious acid. Selenium and tellurium are precipitated by sulfur dioxide from a hydrochloric acid solution. The elements are filtered, washed and dissolved in hydrochloric acid containing sufficient nitric acid to effect solution and then evaporated to dryness on the water bath.

Procedure.—The material is dissolved in hydrochloric acid or in a ten per cent solution of potassium hydroxide, using 2 ml. per 0.2 gram of oxide. The solution, if alkaline, is slightly acidified with hydrochloric acid and then diluted to 200 ml. with boiling water. Dilute ammonium hydroxide is now added in slight excess, and is followed by the faintest excess of acetic acid. Crystalline tellurium dioxide separates out completely on cooling and can be brought on a Gooch crucible, dried at 105° C., and weighed.

NOTES. Tellurium.—The element dissolves in hot concentrated hydrochloric acid. On dilution of the solution a precipitation of H_2TeO_3 occurs. Treated with concentrated nitric acid or aqua regia H_2TeO_4 forms. With sulfuric acid the compound H_2TeO_3 forms and SO_2 is evolved. Tellurium is insoluble in carbon disulfide. The oxides TeO and TeO_2 are soluble in acids, TeO_3 being not readily soluble. All the oxides dissolve in hot potassium hydroxide solutions.

Care must be exercised to avoid overheating acid extracts in the preparation of the sample, since loss by volatilization is apt to occur; this is especially true of the halogen compounds of selenium and tellurium, the former being more volatile than the latter.

Fusion Method.—The finely powdered substance is intimately mixed with about five times its weight of a flux of sodium carbonate and nitrate (4 : 1) and heated gently in a nickel crucible, gradually increasing the heat, until the charge has fused. When

[10] Hydrazine hydrochloride is prepared ordinarily from the sulfate according to the directions given in "Organic Chemical Reagents," Vol. III, page 42, University of Illinois Bulletin, Vol. 19, No. 6, 1921. Hydrazine sulfate is conveniently made from sodium hypochlorite and ammonia. Organic Syntheses, Wiley & Co., Vol. II, pages 37–40, 1922.

[11] Am. J. Sci. (4), 28, 112 (1909).

the molten mass appears homogeneous, it is cooled and extracted with water. Sodium selenate and tellurate pass into solution and are separated from most of the heavy metals. The water extract is acidified with hydrochloric acid and boiled until no more free chlorine is evolved. (Test with starch iodide paper. Cl = blue color.) Metallic selenium and tellurium may be precipitated by passing sulfur dioxide into the hydrochloric acid solution.

Keller has shown that tellurium is not precipitated by SO_2 in concentrated hydrochloric acid solutions (sp.gr. 1.175), whereas selenium is precipitated. Diluted with an equal volume of water (acidity 12 to 20% of above) both tellurium and selenium are precipitated by SO_2.

METHODS AT REFINERIES

COMMERCIAL SELENIUM

A half-gram portion of the material ground to 100 mesh is placed in a 150-ml. beaker, and 10 ml. of water are added, followed by 15 ml. concentrated nitric acid. After the sample has dissolved in the beaker, which is covered with a watch glass, it is evaporated to dryness on the water bath, and taken up in 10 ml. concentrated hydrochloric acid and 20 ml. of water in the cold. The insoluble matter is filtered off and the solution received in a 400-ml. beaker. Sufficient concentrated hydrochloric acid is added to make the solution 70% concentrated hydrochloric acid.

The selenium is precipitated at room temperature by adding a saturated water solution of sulfur dioxide gas, stirring to granulate the selenium. It is recommended that the temperature of the solution be maintained at 60 to 70° F. by placing the beaker in a vessel of running water.

When complete precipitation has been effected and the solution smells strongly of sulfur dioxide, the beaker is removed and allowed to settle for a half hour. The supernatant liquor is decanted through a previously weighed Gooch crucible; the precipitated selenium in the beaker is washed three times with concentrated hydrochloric acid and once with cold water, decanting each time through the crucible. To the precipitate in the beaker 25 ml. of cold water are added, followed by hot water and vigorous stirring until the selenium turns black and granular. It is then filtered, washed with hot water followed by alcohol, and dried at 105° to constant weight. After weighing, the crucible can be gently heated to expel the selenium, in order to obtain a check on its purity. A residue may consist of silica or gold.

Tellurium in the filtrate is recovered by adding three gm. of powdered tartaric acid, diluting with four times its bulk of hot water, then adding 25 ml. ammonium hydroxide and saturating with sulfur dioxide gas. After the sulfur dioxide treatment, which takes but a few minutes, the solution is brought to boiling and allowed to stand for two hours on a hot plate. The granular elementary tellurium is brought on a previously weighed Gooch crucible, washed with hot water, dried at 105° and weighed.

The important laboratory details suggested by Greenwood [12] are:

1. Evaporation of the selenious acid should be made on the water bath rather than on a hot stove in order to avoid loss by volatilization. There is an appreciable loss of selenium dioxide when heated above 100° C. even in the presence of sodium and potassium chlorides. This fact has been verified in Lenher's laboratory.

2. If the temperature of the solution during the precipitation of selenium is above 70° F., the selenium agglomerates and occludes impurities, which cannot be washed out. If the temperature is below 60° F., the precipitation is either incomplete or very much delayed.

3. If the precipitated selenium is not granular, it cakes during the drying and retains moisture even at 110°.

Lead, copper and iron in selenium are determined in a sample of from 10 to 25 g. which is dissolved in 50 to 75 ml. concentrated nitric acid in a 375-ml. casserole and evaporated to dryness. The volatile selenium dioxide is expelled by carefully raising the temperature. The non-volatile residue is dissolved in 10 ml. concentrated nitric acid and 5 ml. concentrated hydrochloric acid, evaporated to 5 ml., when 5 ml. concentrated sulfuric acid are added and evaporated to fumes; it is allowed to cool, 75 ml. of water are added and allowed to stand over night, when the lead sulfate is filtered off and weighed as usual. The filtrate from the lead is treated with hydrogen sulfide, the precipitate is ignited to burn off selenium, tellurium and arsenic, the residue dissolved in nitric acid and the copper determined volumetrically. The filtrate from the precipitation of the copper is boiled to expel the hydrogen sulfide, oxidized by a few crystals of potassium chlorate, and the iron precipitated in the usual manner by ammonia.

An alternate method for the determination of **iron in selenium** is to weigh 10 gm. of the sample into a porcelain dish, ignite at a red heat until the selenium appears to be completely driven off. The residue is sometimes weighed and reported as "non-volatile matter." This residue is fused with sodium carbonate, treated with dilute sulfuric acid, the solution reduced with zinc, and the iron titrated with a weak solution of permanganate.

Insoluble in Commercial Selenium.—Ten to 25 grams are dissolved in a 375-ml. casserole, in concentrated nitric acid, and evaporated to dryness; concentrated hydrochloric acid is added and the silica dehydrated. The insoluble is taken up in hydrochloric acid and water, filtered off, ignited and weighed.

Selenium and Tellurium in Metallic Tellurium.—A 0.5-gram sample of the finely powdered metal is treated with 10 ml. of concentrated sulfuric acid and fumed until all the tellurium has dissolved; after which it is cooled and 20 ml. water and 50 ml. concentrated hydrochloric acid are added.

Selenium is precipitated from the cold solution by adding a saturated solution of SO_2, after which it is filtered through a Gooch crucible, washed three times with hydrochloric acid (2 parts concentrated acid to 1 water), then with hot water and finally with alcohol, dried and weighed. To obtain a check on the purity of the selenium the Gooch crucible is ignited and reweighed.

[12] Eng. Mining J., 100, 1012 (1915).

The tellurium-containing filtrate is diluted to about 700 ml., heated to nearly boiling, a few grams of hydrazine hydrochloride added and a rapid current of sulfur dioxide gas is passed in for 15 minutes, or until the tellurium separates readily; it is then brought on to a Gooch filter, washed with hot water, finally with alcohol. The elementary tellurium is dried for one hour at 105° and weighed.

A selenium and tellurium procedure used for a number of years in one of the refineries consists in dissolving in nitric acid, adding a pinch of salt, evaporating to dryness, taking up in 25 ml. hydrochloric acid (1 : 1) and bringing to boiling. The insoluble matter is filtered off, and the solution treated with a saturated solution of SO_2. A few grams of hydrazine hydrochloride are added and sulfur dioxide again added after which the solution is boiled a few minutes. The precipitated selenium and tellurium are filtered off, dissolved in nitric acid with the addition of a pinch of salt, and the solution evaporated. The residue is taken up in about 200 ml. concentrated hydrochloric acid, the solution again treated with sulfur dioxide and boiled about ten minutes and the selenium brought on a Gooch crucible where it is washed with hot water, then alcohol, dried and weighed.

The tellurium-containing filtrate is diluted with water to three times its volume and saturated with sulfur dioxide; a few grams of hydrazine hydrochloride are added, boiled a few minutes, the tellurium is brought on a Gooch crucible, washed with hot water, then with alcohol, dried and weighed.

Selenium and tellurium in blister or pig copper are commonly determined by the method of Keller, using samples of 50 grams or less.

Selenium and tellurium in electrolytic copper slimes are determined by treating a 0.5-gram sample of the slime in a 250-ml. beaker with 10 ml. concentrated sulfuric acid, heating until the sample is decomposed and nothing remains but a white residue. After cooling, 20 ml. of water are added, followed by 2 ml. concentrated hydrochloric acid, the solution is agitated to coagulate the silver chloride which is then filtered off. The acidity of the filtrate is brought up to about 32% by adding concentrated hydrochloric acid and the selenium and tellurium separated by sulfur dioxide, following the customary procedure.

Selenium in Lead Slimes.—A 2-gram sample is fused with a mixture of 8 grams sodium carbonate and 2 grams nitrate in a nickel crucible. The cold fusion is extracted with water and filtered. The filtrate is acidified with hydrochloric acid and heated until chlorine is expelled. To the solution is added an equal volume of hydrochloric acid, and sulfur dioxide solution is added until the red precipitate becomes granular. The selenium can be brought on an asbestos filter, washed with hydrochloric acid, redissolved in hydrochloric acid and potassium chlorate and reprecipitated by sulfur dioxide solution.

Tellurium in Lead Slimes.—One gram of slimes is treated with a mixture of 10 ml. concentrated sulfuric acid, 10 ml. concentrated nitric acid, and 20 ml. water, and evaporated to fumes. After cooling, 40 ml. water and about 2 grams tartaric acid are added. The solution is boiled and filtered. The residue is washed back into the original beaker, 5 to 10 ml. concentrated sulfuric acid are added, and again evaporated to fumes; 40 ml. of water are added and the solution boiled and filtered. The two filtrates are united and treated with hydrogen sulfide gas. The sulfides are filtered on paper, washed with hydrogen

sulfide water, washed back into the beaker, and a little sodium bicarbonate added followed by about 4 ml. of 10% sodium sulfide solution. The solution is brought to boiling, digested for 12 hours, and filtered through the filter previously used. The sulfide-containing filtrate is acidified with dilute sulfuric acid and treated with hydrogen sulfide gas to render the precipitate granular. The sulfide precipitate, after filtration, is dissolved in nitric acid with the addition of 10 ml. concentrated sulfuric acid and evaporated to fumes of sulfuric acid. It is then diluted with water and boiled after adding about 2 grams of tartaric acid. The solution is cooled, diluted to about 60 ml. with water, and after adding 40 ml. concentrated hydrochloric acid, is again treated with hydrogen sulfide. The precipitate is filtered off, washed with (1 : 1) hydrochloric acid, dissolved in hydrochloric acid and potassium chlorate, warmed gently to expel the excess of chlorine, tartaric acid is again added, any residue filtered off, and the filtrate made strongly acid with hydrochloric acid. The selenium is then precipitated by sulfur dioxide.

The filtrate containing the tellurium is diluted with warm water, and the tellurium precipitated and weighed as usual.

Selenium and Tellurium in Flue Dust.—Two grams are dissolved in hydrochloric acid and potassium chlorate on a water bath, and the excess of chlorine expelled by gentle heat. The insoluble matter is filtered off and washed with concentrated hydrochloric acid, and the filtrate is treated with sulfur dioxide. The selenium and tellurium are brought on a Gooch crucible, washed, then dissolved in hydrochloric acid and potassium chlorate, about 2 grams of tartaric acid are added, followed by concentrated hydrochloric acid, and the selenium is precipitated by sulfur dioxide, filtered off and weighed. The filtrate is diluted to three times its volume with warm water, and the tellurium is precipitated by sulfur dioxide, collected and weighed.

FLUE DUST AND NITER SLAG

Flue dust or niter slag from Doré furnaces can be analyzed for water-soluble selenium and tellurium by boiling a 1-gram sample with water, filtering and washing with hot water, keeping the volume down to 20 ml. To this filtrate are added 200 ml. concentrated hydrochloric acid; the solution is chilled with icewater; and sulfur dioxide is added, the selenium and tellurium being separated by the method of Keller.

The insoluble selenium and tellurium are transferred from the filter to a 50-ml. beaker, concentrated nitric acid and concentrated hydrochloric acid are added, and the solution evaporated at 50° C. or below. It is recommended to evaporate twice more with hydrochloric acid, keeping the temperature at 50° C. or below. The residue is taken up in hydrochloric acid (1 : 2) and filtered, after which 100 ml. concentrated hydrochloric acid are added and the selenium and tellurium in the filtrate are separated by the Keller method.

COMMERCIAL SODIUM SELENITE

To 1 gram of the sample in a 50-ml. beaker are added 10 ml. of water and 5 drops of hydrochloric acid and shaken gently until solution is complete.

After filtering out the insoluble matter, a large excess of concentrated hydrochloric acid is added to the filtrate and selenium is precipitated by sulfur dioxide. In the filtrate from the selenium, the tellurium can be recovered by diluting with warm water and passing in more sulfur dioxide.

SELENIC ACID

Twenty grams of the sample are quickly transferred to a tightly stoppered weighing bottle. After weighing, the acid is put into a liter flask, dissolved in water, and made up to the mark. A 25-ml. portion is measured out and treated with an excess of concentrated hydrochloric acid and the selenium precipitated by sulfur dioxide. If tellurium is present, it can be recovered in the filtrate.

SELENIUM IN GLASS [13]

In ruby glass where selenium is present in quantities of about 0.25%, a two-gram sample is evaporated with hydrofluoric and nitric acids. This evaporation is repeated several times without ignition. The nitrates are then transferred to a small Erlenmeyer flask and the nitric acid destroyed by adding hydrochloric acid. Care must be taken not to boil the solution or selenium will volatilize. A high concentration of the hydrochloric acid must be maintained in order to hold the tellurium in solution. Sulfur dioxide is next added to the solution when elementary selenium is precipitated, washed, dried and weighed as usual.

In glasses where selenium is used as a decolorizer and in which the selenium is present to the extent of less than .0025%, Cousen recommends dissolving the glass in nitric and hydrofluoric acids and determining the selenium colorimetrically by phenylhydrazine hydrochloride, keeping the selenium from precipitating by adding gum arabic. A yellow to a yellowish red solution is obtained which is compared with a color standard containing a known amount of sodium selenite.

SELENIUM AND TELLURIUM IN REFINED COPPER

The success and accuracy of determining small amounts of impurities, is to collect these impurities from a large sample, and to do the necessary chemical work in a small volume of solution.

Ferric hydroxide when precipitated from a copper solution has the peculiar property of forming insoluble compounds with As, Sb, Se and Te.

For complete precipitation, the iron contents must be at least thirty times the combined As, Sb, Se and Te and must be entirely precipitated from the solution.

The iron is best added as ferrous sulfate ($FeSO_4 \cdot 7H_2O$), dissolved in water and oxidized to the ferric salt with HNO_3. Roughly the iron content of $FeSO_4 \cdot 7H_2O$ is 20%, or one-fifth of the weight of ferrous sulfate.

Weigh 100 grams of drillings into a 1300 ml. beaker, cover with water and add gradually 350 ml. HNO_3 (sp.gr. 1.42). When the copper is in solution, boil

[13] Method furnished by the Corning Glass Works.

out all red fumes, dilute to 700 ml. with warm water and neutralize with NH_4OH until just enough copper hydroxide has been formed to cover the bottom of the beaker; then add the required amount of oxidized ferrous sulfate in solution. Stir well, dilute to 900 ml. and boil for at least one hour, settling on the warm plate over night. Filter on a 15 cm. filter.

Treat the filtrate with ammonia until a precipitate of copper hydroxide has formed to cover the bottom of the beaker; half the quantity of oxidized $FeSO_4 \cdot 7H_2O$ added previously, is again added and the solution boiled for one hour, allowing to settle over night on the warm plate. Filter on a 15 cm. filter. It is absolutely necessary that no iron salts be left in this filtrate, either in solution, or as hydrate, therefore, this filtrate had best be tested with ammonia and refiltered on a 15 cm. filter. The three precipitates on the 15 cm. papers are treated as one, dissolved in the least quantity of warm H_2SO_4 (1:1), the papers washed well with hot dilute H_2SO_4 (1:20) and filtered into a 600 ml. beaker. Make strongly ammoniacal, boil well and filter, washing the precipitate well and free from the folds into the apex of the filter. Refilter the filtrate to catch any iron that has washed through. The papers are spread open and the precipitates dissolved in 25 ml. warm HCl (1:1) in a 250 ml. beaker, using as little hot water as possible to remove the yellow stains.

Filter the solution into a 400 ml. beaker, washing with as little hot water as possible. To the filtrate add four times its volume of concentrated HCl and cool.

Add a saturated water solution of SO_2 to precipitate the selenium.

Filter off the precipitated Se on a tared Gooch crucible, wash with cold water and alcohol, dry at 60° C. for two hours, then at 105° C. to constant weight.

Weigh as metallic Se.

Expel the Se from the crucible and reweigh as a check on the weight and the purity of the precipitate.

TELLURIUM

To the filtrate from the precipitated Se, add 2 grams of tartaric acid in order to keep the Sb in solution, dilute to 600 ml. with hot water, add 50 ml.[14] concentrated NH_4OH, and saturate the solution with SO_2 gas. Boil for two minutes and allow to settle 4–6 hours.

Filter the Te on a tared Gooch crucible, wash with hot water and finally with alcohol, dry at 115° C. to constant weight.

Weigh as metallic Te.

[14] Te is best precipitated by SO_2 gas in a 20–30% HCl solution and the strong (80%) HCl solution from the Se precipitation is best neutralized to 25–30%, by the use of ammonia.

VOLUMETRIC DETERMINATION OF SELENIUM AND TELLURIUM

IODOMETRIC DETERMINATION OF SELENIC, OR TELLURIC ACID—REDUCTION WITH HYDROCHLORIC ACID AND DISTILLATION

The method depends upon the reduction of selenic or telluric acid to selenious or tellurious acid by heating with hydrochloric acid, the evolved chlorine being a measure of the acids in question. The chlorine absorbed in potassium iodide solution liberates its equivalent of iodine, which may readily be determined by titration with standard thiosulfate. The following reactions illustrate the change that takes place:

$$K_2SeO_4+4HCl=2KCl+H_2SeO_3+H_2O+Cl_2,$$
$$K_2TeO_4+4HCl=2KCl+H_2TeO_3+H_2O+Cl_2,$$

$1\ Cl.=1\ I=\frac{Se}{2}$ or $\frac{Te}{2}=63.75$ grams Te or 39.6 grams Se per liter normal solution.

According to Gooch and Evans over 30% of strong hydrochloric acid (sp.gr. 1.20) should be present. Dilute hydrochloric acid having a strength of 10% of HCl, (sp.gr. 1.2), does not react with liberation of chlorine. Care must be taken not to prolong the boiling after the solution reaches a concentration of half strength, since over-reduction may take place and the metals be liberated.

Procedure.—The sample containing the selenate or tellurate is treated with 75 ml. of hydrochloric acid, containing 25 ml. of concentrated HCl, sp.gr. 1.20, per 0.2 gram of the oxides, in a distillation flask connected with a Drexel wash bottle receiver, water cooled, and charged with potassium iodide solution. A current of CO_2 is passed into the flask to sweep the liberated chlorine into the iodide solution. The sample is boiled until nearly one-third its volume has distilled into the receiver. The liberated iodine is titrated with standard thiosulfate. One ml. N/10 $Na_2S_2O_3=0.00396$ gram Se or 0.006375 gram Te.

Other than a few corrections suggested by Dr. W. R. Schoeller, with several minor additions, the Editor has retained the greater part of the original chapter by the late Dr. Victor Lenher. The new material is largely from reprints (Ind. Eng. Chem.) sent to the Editor by Dr. Lenher.

SILICON[1]

Si, *at.wt.* 28.06; *sp.gr. amor.* 2.00.; *crys.* 2.49; *m.p.* 1420° C.; *oxides* SiO, SiO_2

Silicon stands next to oxygen in abundance, occurring only in combined form. The oxides quartz, tridymite (silica), SiO_2 occur in great quantities. Silicates occur in all of the common rocks except in carbonates. It has been estimated that the earth's crust is composed of more than 27% of silicon, combined in one form or other.

DETECTION

The finely ground sample together with a small quantity of powdered calcium fluoride is placed in a small lead cup 1 cm. in diameter and depth (see Fig. 96), and a few drops of concentrated sulfuric acid added. A lead cover, with a small aperture, is placed on the cup, and the opening covered with a piece of moistened black filter paper. Upon this paper is placed a moistened pad of ordinary filter paper. The cup is now gently heated on the steam bath. At the end of about ten minutes a white deposit will be found on the under side of the black paper, at the opening in the cover, if an appreciable amount of silica is present in the material tested.

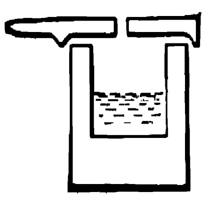


Fig. 96. Lead Cup for Silica Test.

A silicate, fused with sodium carbonate or bicarbonate in a platinum dish and the carbonate decomposed by addition of hydrochloric acid with subsequent evaporation to dryness, will liberate silicon as silicic anhydride, SiO_2. The silica placed in a platinum dish is volatilized by addition of hydrofluoric acid, the gaseous silicon fluoride being formed. A drop of water placed in a platinum loop, held in the fumes of SiF_4, will become cloudy owing to the formation of gelatinous silicic acid and fluosilicic acid,

$$3SiF_4+3H_2O=H_2SiO_3+2H_2SiF_6.$$

[1] Silicon was first obtained in 1823 by Berzelius by the action of potassium on silicon tetrachloride. It may be made by reduction of SiO_2 with carbon at high temperature. It is used alloyed with iron (duriron) in acid resisting materials, and in small amounts in steel used for transformer coils.

If a silicate is fused in a platinum loop with microcosmic salt, the silica floats around in the bead, producing an opaque bead with weblike structure upon cooling.

ESTIMATION

The gravimetric procedure is the only satisfactory method for the estimation of silica. The substance in which the element is combined as an oxide or as a silicate is decomposed by acid treatment or by fusion with an alkali carbonate or bicarbonate, the material taken to dryness with addition of hydrochloric acid, whereby the compound silica is liberated. If other elements are present the silica is volatilized by addition of hydrofluoric acid and estimated by the loss of weight of the residue.

Combined as SiO_2 and in silicates the element is very widely distributed in nature and is a required constituent in practically every complete analysis of ores, minerals, soils, etc. It is present in certain alloys, ferro-silicon, silicon carbide, etc.

The element is scarcely attacked by single acids, but is acted upon by nitric-hydrofluoric acid mixture. It dissolves in concentrated alkali solutions. Silica is decomposed by hydrofluoric acid and by fusion with the fixed alkali carbonates or hydroxides.

Silicon is isolated as SiO_2 in the initial stage of analysis and if present in the material examined boron, columbium, tantalum and tungsten will accompany silica. Lead, barium and calcium will be found with this residue if sulfates are present. Tin, antimony and bismuth are apt to contaminate the silica if these are present. Silica is determined by difference after volatilization with HF and H_2SO_4 treatment.

PREPARATION AND SOLUTION OF THE SAMPLE

General Considerations.—The natural and artificially prepared silicates may be grouped under two classes: 1. Those which are decomposed by acids. 2. Silicates not decomposed by acids. The minerals datolite, natrolite, olivine and many basic slags are representative of the first class, and feldspar, orthoclase, pumice and serpentine are representative of silicates not decomposed by acids. (See more complete list under List of More Important Silicates, page 797.) The first division simply require an acid treatment to isolate the silica, the latter class require fusion with a suitable flux.

In technical analysis, in cases where great accuracy is not required, the residue remaining, after certain conventional treatments with acids, is classed

as silica. This may consist of fairly pure silica or a mixture of silica, undecomposed silicates, barium sulfate and certain acid insoluble compounds. For accurate analyses this insoluble residue is not accepted as pure silica, unless impurities, which are apt to be found with the silica residue, are known to be absent from the material under examination.

Although the procedure for isolation of silica is comparatively simple, errors may arise from the following causes:

(1) Imperfect decomposition of the silicate.

(2) Loss of the silica by spurting when acid is added to the carbonate fusion.

(3) Slight solubility of silica, even after dehydration, especially in presence of sodium chloride and magnesia.

(4) Loss due to imperfect transfer of the residue to the filter paper.

(5) Mechanical loss during ignition of the filter and during the blasting, due to the draft whirling out the fine, light silica powder from the crucible.

(6) Error due to additional silica from contaminated reagents or from the porcelain dishes or glassware in which the solution was evaporated. A blank of 0.01% on the sodium carbonate will make an error of 0.1% per gram sample in an ordinary fusion where 10 grams of the flux are required.

(7) Error due to loss of weight of the platinum crucible during the blasting.

(8) Incomplete removal of water, which is held tenaciously by the silica. Furthermore, weighing of the residue should be done quickly, as the finely divided silica tends to absorb moisture. Ignition to constant weight at 1200° C. is necessary.

(9) Expulsion of products by HF other than silica such as trivalent arsenic and boron. These substances should be removed before the HF treatment of the residue.

(10) Formation of sulfates in the residue, not originally present, for example the change of $KAlSi_3O_8$ to K_2SO_4 and Al_2O_3.

(11) Combination of substances with silica preventing its volatilization. For example alkaline earths forming silicates during the heating of the residue. When fusions are made with alkali salts, care should be exercised to completely remove these during the acid treatment of the silica.

(12) In presence of fluorides loss of silica will occur during the acid attack of the material, so that special treatment is necessary to prevent loss. If boron is present it is volatilized as $B(OCH_3)_3$ by treating the ore with methyl alcohol and sulfuric acid previous to the dehydration of silica. If tungsten is present the volatilization of silica must be conducted at a temperature below 850° C. at which temperature tungsten oxide volatilizes.

Decomposition of silicates is best effected by fusions with alkali fluxes followed by attack with acids.

PREPARATION OF THE SUBSTANCE FOR DECOMPOSITION

If the material is an ore or mineral it is placed on a steel plate within a steel ring and broken down by means of a hardened hammer to small lumps and finally to a coarse powder. A quartered portion of this is air dried and ground as fine as possible in an agate mortar and preserved in a glass-stoppered bottle for analysis.

Analyses are based on this air-dried sample. If moisture is desired it may be determined on a large sample of the original material. Hygroscopic moisture is determined on the ground, air-dried sample, by heating for an hour at 105 to 107° C.

List of Most Important Silicates. *Silicates Decomposed by Acids.*—Allanite; allophane; analcite; botryolite; brewsterite; calamine; chabasite; croustedtitite; datolite (hydrated silicate and borate of Ca with Al and Mg); dioptase; eulytite; gadolinite; gahlenite; helvite; ilvaite (silicate ferrous and ferric iron with Al_2O_3, CaO and MgO); laumonite; melinite; natrolite (hydrated silicate of Al and Na with Fe and CaO); okenite; olivine (silicate of Fe and Mg); pectolite; prehenite (hydrated Al and Ca silicate with Fe, Mn, K, Na, etc.); *teproite; wernerite; woolastonite; zaolite.*

Silicates Undecomposed by Acids.—Albite; andalusite; augite; axinite; beryl; carpholite: cyanite; diallage, epidote (silicate of Fe, Al and Ca with FeO, Mn, Mg, K, Na); euclase; feldspar (silicate of K, Na, Al, Fe, Ca and Mg); garnet; iolite; labradorite; (micas of K and Mg); orthoclase; petalite; pinite, prochlorite; pumice; serpentine; sillimanite, talc, topaz, tourmaline (Fe_2O_3, FeO, Mn, Al, Ca, Mg, K, Na, Li, SiO_2, B_2O_3, P_2O_5, F); vesuvianite.

DECOMPOSITION OF THE MATERIAL, GENERAL PROCEDURES

Silicates Decomposed by Acids

Acid Extraction of the Silicates.—0.5 to 1 gram of the finely pulverized material placed in a beaker or casserole is treated with 10 to 15 ml. of water and stirred thoroughly to wet the powder.[2] It is now treated with 50 to 100 ml. of concentrated hydrochloric acid and digested on the water bath for fifteen or twenty minutes with the beaker or casserole covered by a watch-glass. If there is evidence of sulfides (pyrites), etc., 10 to 15 ml. of concentrated nitric acid are now added and the containing vessel again covered. After the reaction has subsided, the glass cover is raised by means of riders and the mixture evaporated to dryness on the water bath. (This evaporation may be hastened by using a sand bath, boiling down to small bulk at comparatively high temperature, then to dryness on the water bath. Decomposition is complete if no gritty particles remain. A flocculent residue will often separate out during the digestion, due to partially dehydrated silicic acid; hydrated silicic acid, $Si(OH)_4$ is held in solution.) The silicic acid is converted to silica, SiO_2, the residue taken up with dilute hydrochloric acid, silica filtered off, washed with water acidified with hydrochloric acid, and estimated according to the procedure given later.

Silicates Not Decomposed by Acids

Fusion with Sodium Carbonate or Sodium Bicarbonate.—0.5 to 1 gram of the air-dried, pulverized sample is placed in a large platinum crucible or dish in which has been placed about 5 grams of anhydrous sodium carbonate. The sample is thoroughly mixed with the carbonate by stirring with a dry glass rod, from which the adhering particles are brushed into the crucible. A little carbonate is sprinkled on the top of the mixture and the receptacle covered. It is heated to dull redness for five minutes and then gradually

[2] Water is added to the sample and then acid, as concentrated acid added directly would cause partial separation of gelatinous silicic acid, which would form a covering on the undecomposed particles, protecting them from the action of the acid.

heated up to the full capacity of a Méker burner. When the mix has melted to a quite clear liquid, which generally is accomplished with twenty minutes of strong heating, a platinum wire with a coil on the immersed end is inserted in the molten mass, and this allowed to cool. The fusion is removed by gently heating the crucible until the outside of the mass has melted, when the charge is lifted out on the wire, and after cooling disintegrated by placing it in a beaker containing about 75 ml. dilute HCl (1 part HCl to 2 parts H_2O), covering the beaker to prevent loss by spattering. The crucible and lid are cleaned with dilute hydrochloric acid, adding this acid to the main solution. When the disintegration is complete, the solution is evaporated to dryness and silica is estimated according to directions given later.

If decomposition is incomplete, gritty material will be found in the beaker upon treatment of the fusion with dilute acid. If this is the case, it should be filtered off and fused with a second portion of sodium carbonate, and the fusion treated as directed above.[3]

SPECIAL PROCEDURES FOR DECOMPOSING THE SAMPLE

Treatment of Iron and Steel for Silica.—One gram of pig-iron castings, or 5 grams of steel are taken for analysis, both the fine and coarse drillings being taken in about equal proportion. (Fine particles contain more silicon than the coarse chips.) Twenty to 50 ml. of dilute nitric acid (sp.gr. 1.135) are added to the sample in a 250-ml. beaker or small casserole, and this covered. If the action is violent, cooling, by placing the beaker in cold water until the violent action has subsided, is advisable. Twenty ml. of 50% sulfuric acid are added and the solution evaporated on the hot plate to SO_3 fumes. After cooling, 150 ml. of water are added and 2 to 5 ml. dilute sulfuric acid. The mixture is heated until the iron completely dissolves and the silica is filtered off onto an ashless filter, washed with hot dilute hydrochloric acid (sp.gr. 1.1), and with hot water until free from iron. The residue is ignited and the silica estimated according to the procedure given later.

Pig iron and cast iron may be decomposed by digestion with a mixture of 8 parts by volume of HNO_3 (sp.gr. 1.42), 5 parts of H_2SO_4 (sp.gr. 1.84), and 17 parts of water.

Steel and wrought iron may be disintegrated by a mixture of 8 parts by volume of HNO_3 (sp.gr. 1.42), 4 parts H_2SO_4 (sp.gr. 1.84), and 15 volumes of water.

Ferro Silicons.—Dilute hydrochloric acid, 1 volume of acid (sp.gr. 1.19), with 2 volumes of water is a better solvent than the concentrated acid.

[3] Fusions with soluble carbonates are generally best effected with the sodium salt, except in fusions of niobates, tantalates, tungstates, where the potassium salt is preferred on account of the greater solubility of the potassium compounds. Sodium alone has an advantage over the mixed carbonates, $Na_2CO_3+K_2CO_3$, as silica has a high melting-point and a flux, which fuses at 810° C., is more apt to cause disintegration of the silicate than the mixture, which melts at 690° C.

Prolonged blasting is undesirable, as it renders the fusion less soluble. Aluminum and iron are also rendered difficultly soluble, when their oxides are heated to a high temperature for some time.

If the melt is green, it is best to dissolve out the adhering melt from the crucible with dilute nitric acid, as a manganate (indicated by the color), if present, will evolve free chlorine by its action on HCl and this would attack the platinum.

Steels Containing Tungsten, Chromium, Vanadium and Molybdenum.—Fusion with potassium acid sulfate, $KHSO_3$, in a platinum dish, or sodium peroxide in a nickel crucible will generally decompose the material. Sodium peroxide is of special value in decomposing chromium alloys.

Silicon Carbide, Carborundum.—This is best brought into solution by fusion with potassium hydroxide in a nickel crucible or by fusion with Na_2O_2 in a pure iron crucible. Sulfuric, hydrochloric, nitric acids, or aqua regia have no effect upon this refractory material.

Sulfides, Iron Pyrites, etc.—These require oxidation with concentrated nitric acid or a mixture of bromine and carbon tetrachloride, followed by nitric, exactly according to the procedure given for solution of pyrites in the determination of sulfur. The sample is taken to dryness and then hydrochloric acid added and the solution again evaporated. The residue is dehydrated and silica determined as usual.

Slags and Roasted Ores.—Digestion with hydrochloric acid according to the first general procedure is best. The addition of nitric acid to decompose sulfides may be necessary.

Decomposition of silicates by fusion with lead oxide (method of Jannasch), and calcium carbonate and ammonium chloride (method of Hillebrand), are of value when sodium is desired on the same sample. The procedures are given under chapters on Sodium and Potassium.

NOTE.—K_2CO_3 is preferred to Na_2CO_3 for fusion of tungstates, niobates and tantalates on account of the greater solubility of the potassium salts. For corundum and alumina silicates Na_2CO_3 is preferred as double salts of potassium and aluminum are less soluble than the sodium salts.[4]

Fluorides of silicon are fused with boric acid, BF_3 is volatized, SiF_4 is not formed. P. Jannasch.[5]

Fluorides.[6]—In presence of fluorides the melt is extracted with water (an acid extraction would volatilize some of the silica), and the extract filtered off from the insoluble carbonates. To the filtrate is added about 5 grams of solid ammonium carbonate, and the mix warmed to 40° C. and allowed to stand for several hours. The greater part of the silica is precipitated. This is filtered off and washed with water containing ammonium carbonate. Preserve this with the insoluble carbonate for later treatment. The filtrate, containing small amounts of silicic acid, is treated with 1 to 2 ml. of ammoniacal zinc oxide solution (made by dissolving C.P. moist zinc oxide in ammonia water). The mixture is boiled to expel ammonia and the precipitate of zinc silicate filtered off. The precipitate is washed into a beaker through a hole made in the filter, and the adhering material dissolved off with dilute HCl, enough being added to dissolve the remaining residue. This is evaporated to dryness and silica separated as usual. Meantime the insoluble carbonate is dissolved with HCl, evaporated to dryness and any silica it contains recovered. Finally all three portions of silica are combined, ignited and silica estimated as usual.

[4] J. L. Smith, Am. J. Sci. (2), 40, 248, 1865. Chem. News, 12, 220 (1865).
[5] P. Jannasch, Ber., 28, 2822 (1896).
[6] Sodium bicarbonate may be used in place of the carbonate with excellent results. See also "Determination of Silica in Presence of Fluorspar," later in this chapter.

SEPARATIONS

Separation of Silicon.—This is accomplished in the initial steps of the general procedure of analysis by dehydration by means of sulfuric acid or perchloric acid. Silica is now treated with HF and volatilized and determined by loss of weight of the acid insoluble residue.

Separation of Lead.—Lead sulfate present in the insoluble residue may be extracted by a solution of concentrated ammonium acetate slightly acid with acetic acid. Silica remains undissolved.

Insoluble Residue.—After removal of silica and lead there may remain a residue which may contain columbium, tantalum, titanium, tungsten, barium, calcium, strontium, antimony, bismuth, tin, etc.

Boron.—The presence of boron in the residue will cause an error in the silicon determination since it will volatilize with the HF treatment. This may be separated by volatilization as $B(OCH_3)_3$ with alcohol and acid before expulsion of silica with HF. See chapter on Boron.[7]

Silicon in Fluorspar.—A special procedure will be found later in this chapter. The presence of fluoride requires a special procedure to avoid loss of silica during decomposition of the material.

PROCEDURE FOR THE DETERMINATION OF SILICON AND SILICA

As has been stated, the gravimetric method for determination of silica is the only satisfactory procedure for estimation of this substance.

Extraction of the Residue—First Evaporation.—The residue, obtained by evaporation of the material after decomposition of the silicate, by acids or by fusion, as the case required, is treated with 15–25 ml. of hydrochloric acid (sp.gr. 1.1) covered and heated on the water bath 10 minutes. After diluting with an equal volume of water, filtration is proceeded with immediately, and the silica is washed with a hot solution consisting of 5 ml. hydrochloric acid (sp.gr. 1.2) to 95 ml. of water and finally with water. This filtration may be performed with suction. The filtrate and washings are evaporated to small volume on a sand bath and then to dryness. This contains the silica that dissolved in the first extraction.

Second Evaporation.—The residue obtained from evaporation of the filtrate is dehydrated for 2 hours at 105–110° C.[8] and extracted with 10 ml. of hydro-

[7] In presence of tungsten the temperature should be kept below 850° during volatilization of silica with HF.

[8] Dehydration of silica is aided by the presence of lime and retarded by magnesia. In presence of the latter a soluble magnesium silicate will form if the dehydration is conducted at a temperature much above 110° C., hence it is better to avoid this by taking more time and heating to 100 or 105° as recommended.

Sodium chloride has a solvent action on silica, the reaction of HCl on sodium silicate being reversible; $2HCl+Na_2SiO_3 \rightleftarrows 2NaCl+H_2SiO_3$. An evaporation of the filtrate to dryness will recover the greater part of the silica thus dissolved.

chloric acid (sp.gr. 1.1) covered and heated on the water bath for ten minutes diluted to 50 ml. with cold water and filtered immediately, without suction. The residue is washed with cold water containing 1 ml. concentrated hydrochloric acid to 99 ml. water, the washed residue containing practically all[9] the silica, that went into solution in the first extraction, is combined with the main silica residue. This is gently heated in a platinum crucible until the filters are thoroughly charred, and then ignited more strongly to destroy the filter carbon and finally blasted over a Méker burner for at least thirty minutes, or to constant weight, the crucible being covered. After cooling, the silica is weighed. For many practical purposes this residue is accepted as silica, unless it is highly colored. For more accurate work especially where contamination is suspected (silica should be white), this residue is treated further.

Estimation of True Silica.—Silica may be contaminated with $BaSO_4$, TiO_2, Al_2O_3, Fe_2O_3, P_2O_5 combined (traces of certain rare elements may be present). The weighed residue is treated with 3 ml. of water, followed by several drops of concentrated sulfuric acid and 5 ml. of hydrofluoric acid, HF (hood). After evaporation to dryness, the crucible is heated to redness and again cooled and weighed. The loss of weight represents silica, SiO_2.[10]

NOTES.—Lenher and Truog make the following observations for determining silica:[11]

1. In the sodium carbonate fusion method with silicates, there is always a non-volatile residue when the silica is volatilized with hydrofluoric and sulfuric acids.

2. The non-volatile residue contains the various bases, and should be fused with sodium carbonate and added to the filtrate from the silica when the bases are to be determined.

3. In the dehydration of the silica from the hydrochloric acid treatment of the fusion, the temperature should never be allowed to go above 110° C.

4. Dehydrated silica is appreciably soluble in hydrochloric acid of all strengths. With the dilute acid used, this error is almost negligible

5. Dehydrated silica is slightly soluble in solutions of the alkaline chlorides As sodium chloride is always present from the sodium carbonate fusion, an inherent error is obviously thus introduced.

6. The dehydrated silica along with the mass of anhydrous chlorides must not be treated first with water, since hydrolysis causes the formation of insoluble [illegible] of iron and aluminum, which do not dissolve completely in hydrochloric acid.

7. Hydrochloric acid (sp.gr. 1.1) in minimum amount should be [illegible] the dehydrated chlorides and should be followed by water to bring the [illegible] 50 ml., after which the silica should be filtered off as quickly as possible.

8. Pure silica comes quickly to constant weight on ignition. [illegible] silica frequently requires long heating with the blast flame in [illegible] weight, and is then commonly hydroscopic.

9. Evaporations of the acidulated fusion in porcelain give [illegible] as when platinum is used.

10. Filtration of the main bulk of the silica after one [illegible] much as the silica is removed at once from the solutions which act [illegible]

11. Dehydration of the silica under reduced pressure has no [illegible] common evaporation at ordinary atmospheric pressure

[9] Not more than 0.1% of the original SiO_2 may still be in solution

[10] Silicic acid cannot be completely dehydrated by a single evaporation [illegible] nor by several such treatments, unless an intermediate filtration of silica [illegible] however, silica is removed and the filtrate again evaporated to dryness and [illegible] heated, the amount of silica remaining in the acid extract is negligible (See [illegible] W. F. Hillebrand, J. Am. Chem. Soc., 24, 368 (1902)) Boron, if present, will [illegible] with silica. Its removal with methyl alcohol should be made before [illegible] silica. See Introductory Section.

[11] Victor Lenher and Emil Truog, J. Am. Chem Soc , 38, 1050 (1916).

12. Excessive time of dehydration, viz., four hours, possesses no advantages.
13. Excessive amounts of sodium carbonate should be avoided, since the sodium chloride subsequently formed exerts a solvent action on the silica. The best proportions are 4–5 sodium carbonate to 1 of silicate. Less than 4 parts of sodium carbonate is frequently insufficient completely to decompose many silicates.
14. The non-volatile residue has been found to be invariably free from sodium. Pure silica, on fusion with sodium carbonate, subsequently gives no non-volatile residue.

PERCHLORIC ACID AS A DEHYDRATING AGENT [12]

Procedure for Metals and Alloys.—Weigh out a sample corresponding to about 10 mg. of silica, using a 100 or 150 ml. beaker. Dissolve it in either nitric or hydrochloric acid, depending on which reagent is more suitable for effecting solution. For steel, 20 to 40 ml. of dilute nitric acid (sp.gr. about 1.17) will be found convenient. After the action has ceased add 8 to 10 ml. of perchloric acid (60 to 70%) for each gram of metal dissolved. The amount of acid required depends upon the solubility of the metal perchlorate in hot concentrated perchloric acid. In the case of aluminum and its alloys it is necessary to use as much as 15 ml. of perchloric acid per gram of sample. Support the cover glass on glass hooks to facilitate evaporation, place the beaker on the hot-plate and evaporate to copious fumes of perchloric acid. Remove the glass hooks to prevent unnecessary loss of acid and boil 15 to 20 minutes, so that the acid refluxes down the side of the beaker. Especial care must be taken never to allow the boiling contents of the beaker to become solid, since if this occurs the separation of silica is always incomplete. If there is a tendency for much insoluble perchlorate to separate out, either the heating is not properly regulated or insufficient acid is present. In the case of aluminum, however, there is always a considerable amount of insoluble perchlorate. As the solution cools it usually becomes completely solid. Dilute with 4 or 5 times its volume of water, heat to boiling, filter off the silica, wash it with very dilute hydrochloric acid and finally with water, ignite and weigh as usual. Treat the precipitate with hydrofluoric and sulfuric acids, ignite and weigh the residue to determine the weight of pure silica. This correction is usually very small.

High per cent ferrosilicon is not decomposed by perchloric acid.

Procedure for Limestone and Soluble Silicates.—In a 100 to 150 ml. beaker dissolve about 0.5 g. of the material in a mixture of 5 ml. perchloric acid and 10 ml. of water. If the silica content is very high, it is advisable to use more acid. Evaporate to dense fumes of perchloric acid and follow the procedure for metals described above. Insoluble silicates must first be fused with sodium carbonate as usual.

DETERMINATION OF SILICA IN PRESENCE OF FLUORSPAR

When a silicate containing a fluoride is fused with boric oxide no loss of silica occurs, since the fluorine is expelled as boron trifluoride.[13] The method is based on this principle.

[12] Willard and Cake, J. Am. Chem. Soc., 42, 2208 (1920).
[13] Jannasch and Weber, Ber., 32, 1670 (1899).

The procedure recommended by Schrenk and Ode [14] is as follows:

Procedure.—A 0.5 gram sample of finely ground material is treated with 15 ml. of 20% perchloric acid saturated with boric acid at 50° C. The ore is digested with this solution in a pyrex beaker and heated until fumes of perchloric acid are evolved for 4 to 5 minutes. A few ml. of water are now added and the fuming repeated for 4–5 minutes. The residue is diluted with about 75 ml. of water and the solution heated and the silica and insoluble matter filtered off. The filter paper is washed, first with dilute solution of perchloric acid and finally with hot water to remove free calcium salts (as shown by tests with ammonium oxalate). The paper and residue is ignited in a platinum crucible, two drops of concentrated sulfuric acid added and the residue ignited to constant weight. The silica is now volatilized by treatment with hydrofluoric acid by the customary procedure for silica, and silica estimated by the loss of weight.

NOTES.—The method is rapid and accurate and solves a problem that was formerly considered a difficult one and entailed a laborious procedure for separation, as the customary methods could not be employed, since the presence of HF would cause a loss of silica.

By the Berzelius-Hillebrand Method [15] the material (0.5 g.) is fused with Na_2CO_3 in a platinum crucible, the cooled cake extracted of silica by digesting with water (100 ml.) and the insoluble carbonates filtered off. The silica in the water extract is precipitated by addition of an excess of solid ammonium carbonate (5 g. or more), and allowing to stand for several hours, and filtering. The silica that still remains in the filtrate is recovered by precipitation with ammoniacal zinc oxide solution, this precipitate is filtered off, and dissolved in dilute HCl, then taken to dryness and the silica separated in the usual way. The silica remaining in the water insoluble carbonate and that precipitated by the ammonium carbonate is now obtained by dissolving the precipitates in HCl, evaporating to dryness and separating the silica by the usual procedure. The total silica residues are now weighed. For further details consult the original work of Hillebrand.

COLORIMETRIC DETERMINATION OF SILICON

The method is applicable to the determination of minute amounts of silica in water and is based on the production of the highly colored yellow silicomolybdic acid when dilute silica solutions are treated with an acid and ammonium molybdate. The color that develops is matched by a standard silica solution treated in the same way or by a known solution of picric acid. E. J. King and C. C. Lucas [16] recommend that 25.6 mg. vacuum-dried picric acid per liter is equivalent to 50 mg. of silica per liter. The picric acid solution is considered a better standard as it is permanent, while the silica solution standard is not.

Procedure.—To 50 ml. of the solution tested are added 2 ml. of a 10% solution of ammonium molybdate and 4 drops of 50% (by volume) sulfuric acid. The yellow color which develops reaches its maximum in less than ten minutes and remains constant for some time. Appropriate dilutions of the picric acid standard are made and the solutions are compared in a colorimeter or in Hehner tubes.

[14] W. T. Schrenk and W. H. Ode, Ind. Eng. Chem., Anal. Ed. 1, 201 (1929).
[15] W. F. Hillebrand, U. S. Geol. Survey, Bull. 700, p. 222 (1919).
[16] King and Lucas, J. Am. Chem. Soc., 50, 2395 (1928).

RAPID METHOD FOR DETERMINATION OF SILICON

A two (0.9344 gram) to five (2.3360 grams) factor weight sample is transferred to a 300 ml. porcelain casserole and dissolved by addition of from 30 to 50 ml. of hydrochloric acid (sp.gr. 1.19), the casserole being covered with a clock-glass cover and warmed until the reaction is complete. Several ml. of nitric acid (sp.gr. 1.42) and from 40 to 60 ml. of sulfuric acid (1:1) are added and the solution evaporated until fumes of sulfur trioxide are evolved. The solution is allowed to cool somewhat, 200 ml. of warm water are added and the liquid is boiled for several minutes or until all salts have dissolved. The silica is filtered on an 11 cm. blue ribbon paper, containing some ashless paper pulp, and washed thoroughly with hot water.

The paper and precipitate are ignited in a small platinum crucible, first at a low temperature until the carbon of the filter paper has been oxidized, and finally at 1050 to 1100° C. The crucible and its contents are cooled in a desiccator and weighed. One or two drops of sulfuric acid (sp.gr. 1.84) and several ml. of pure hydrofluoric acid (48%) are added and after having evaporated the solution until all sulfuric acid has been expelled the crucible is again ignited and weighed. The difference between the first and second weights, divided by 2 or 5 and multiplied by 100, gives the percentage of silicon in the sample.

If desired, perchloric acid (60%) may be used to dehydrate the silica in place of the sulfuric acid, in which case 20 ml. of the 60% acid are required for a two factor weight sample. Since the perchlorate salts are readily soluble and cause no trouble during the evaporation to fumes, a determination may be completed in about one-half the time as when using sulfuric acid. Perchloric acid serves to render soluble any insoluble chromium carbide present. Also, the results obtained by the use of perchloric acid are of a higher degree of accuracy than those with sulfuric acid. The sample may be dissolved by direct treatment with the perchloric acid and the solution evaporated to strong fumes of perchloric acid. The cover glass and sides of the casserole are rinsed down with water, and the evaporation to strong fumes of perchloric acid is repeated. The residue is taken up with 100 ml. of water, the solution filtered and the determination completed as described in the second paragraph.

ANALYSIS OF SILICATE OF SODA

DETERMINATION OF Na_2O

Five grams of the sample are dissolved in about 150 ml. of water and heated; 1 ml. of phenolphthalein is added and then an excess of standard sulfuric acid from a burette. The excess acid is titrated with standard sodium hydroxide to a permanent pink.

$$H_2SO_4 \times 0.6321 = Na_2O.$$

Silica.—Ten grams of the sample are acidified with hydrochloric acid and evaporated to dryness on the steam bath. The treatment is repeated with additional hydrochloric acid and then the residue taken up with 5 ml. of the acid and 200 ml. of water. The residue is digested to dissolve the soluble salts, filtered, washed and ignited. Silica is determined by loss of weight by volatilization of the silica with hydrofluoric and sulfuric acids. The filtrate is made to 1 liter.

Iron and Alumina.—Five hundred ml. (5 grams) of the filtrate from the silica determination are oxidized with HNO_3 and the iron and alumina precipitated with ammonia, washed, ignited and weighed as Al_2O_3 and Fe_2O_3. The residue is dissolved by digestion with hydrochloric acid or by fusion with sodium acid sulfate, and subsequent solution in hydrochloric acid. Iron is determined by titration in a hot hydrochloric acid solution with standard stannous chloride, $SnCl_2$, solution as usual. If only a small amount of precipitate of iron and alumina is present, as is generally the case, solution by hydrochloric acid is preferable to the fusion with the acid sulfate. The latter is used with larger amounts of the oxides.

Lime, CaO.—This is determined in the filtrate from iron and alumina by precipitation as the oxalate and ignition to CaO.

Magnesia, MgO.—This is determined in the filtrate from lime by precipitation with sodium ammonium phosphate. The precipitate is ignited and weighed as $Mg_2P_2O_7$ and calculated to MgO. Precipitate $\times 0.3621 =$ MgO.

Combined Sulfuric Acid.—One hundred ml. of the filtrate from the silica determination (= 1 gram) is treated with $BaCl_2$ solution and sulfuric acid precipitated as $BaSO_4$.

$$BaSO_4 \times 0.4202 = H_2SO_4 \quad \text{or} \quad \times 0.3430 = SO_3.$$

Sodium Chloride.—Ten grams of the silicate of soda are dissolved in 100 ml. of water and made acid with HNO_3 in slight excess and then alkaline with MgO. Cl is titrated with standard $AgNO_3$ solution.

Water.—This is determined either by difference or by taking 10 grams to dryness and then heating over a flame and blasting to constant weight.

NOTE.—For detailed procedures for each of the above see special subject.

ANALYSIS OF SAND, COMMERCIAL VALUATION

Silica.—Two grams of the finely ground material are fused in a platinum crucible with 10 grams of fusion mixture ($K_2CO_3+Na_2CO_3$) by heating first over a low flame and gradually increasing the heat to the full blast of a Méker blast lamp. When the fusion has become clear it is cooled by pouring on a large platinum cover. The fused mass on the cover and that remaining in the

platinum crucible are digested in a covered beaker with hot hydrochloric acid on the steam bath. The solution is now evaporated to dryness, taken up with a little water and 25 ml. of concentrated HCl and again taken to dryness. Silica is now determined by the procedure outlined under the general method on page 800.

Ferric Oxide and Alumina.—The filtrate is oxidized with crystals of solid potassium chlorate, $KClO_3$, and iron and aluminum hydroxides precipitated with ammonia. The precipitate is filtered, washed, ignited and weighed as $Al_2O_3+Fe_2O_3$.

Calcium Oxide.—To the ammoniacal filtrate 10 ml. of ammonium oxalate solution are added, the solution heated to boiling and the precipitate allowed to settle until cold. The solution should not be over 200 ml. The calcium oxalate is filtered off, washed and ignited. The residue is weighed as CaO.

Magnesium Oxide.—The filtrate from the lime is made strongly ammoniacal and 10 ml. of sodium ammonium phosphate added. The solution during the addition is allowed to stand cold for some time, three to four hours. The precipitate is filtered and washed with dilute ammonia (1 of reagent to 3 parts of water), then ignited and weighed as $Mg_2P_2O_7$. This weight multiplied by $0.3621 = MgO$.

For more detailed directions see the individual subjects under the chapters devoted to the element.

DETERMINATION OF SILICON IN CAST IRON AND STEEL

One gram of pig iron, cast iron, or high silicon iron, or 5 grams of steel, wrought iron, or low silicon iron are taken for analysis. (By taking multiples of the factor weight 0.4693, SiO_2 to Si, the final calculation is simplified.) The sample is placed in a 250-ml. beaker and 20 to 50 ml. of dilute nitric acid added. If the action is violent, cooling the beaker in water is advisable. When the reaction subsides, 20 ml. of dilute sulfuric acid (1 : 1), are added, the mixture placed on the hot plate and evaporated to dense white fumes. The residue is taken up with 150 ml. of water containing 2 to 5 ml. of sulfuric acid and heated until the iron completely dissolves.

The solution is filtered and the silica residue washed first with hot dilute hydrochloric acid (sp.gr. 1.1), and then with hot water added in small portions to remove the iron sulfate. The residue is now ignited and weighed as silica.

Note.—If the ash is colored by iron oxide, silica is determined by difference, after expelling the silica by adding 4 to 5 ml. of hydrofluoric acid and a few drops of sulfuric, taking to dryness and igniting the residue.

The following acid mixtures are recommended by the U. P. Ry. For steel, wrought iron and low silicon iron, 8 parts by volume of HNO_3, sp.gr. 1.42; 4 parts of concentrated H_2SO_4, sp.gr. 1.84; 6 parts HCl, sp.gr. 1.2 and 15 parts by volume of water.

CAUSES OF ERROR IN SILICA DETERMINATIONS

F. G. Hawley (Eng. Mining J., **103**, 541 (1917)) states the following:

It has been shown that there are three main sources of error in the method commonly used for the determination of silica: A plus error from the small amount of SiO_2 from the flux; another plus error due to impurities retained by the SiO_2; and a minus error due to the solubility of SiO_2 in HCl.

By far the largest and most troublesome error is the one due to the solubility of the SiO_2 in the HCl. This error is much greater than most chemists realize.

The amount of freshly precipitated SiO_2 that dissolves in HCl, depends on the following conditions: First, the amount of acid present; second, the strength of the acid; third, the temperature; and fourth, the length of time the silica is in contact with the acid. There may be other conditions governing the solubility of SiO_2 in HCl, but these seem to be the principal ones. By far the most important is the amount of acid used.

Most chemists use acid of about the same strength to treat the dehydrated silica, and the assays are brought to a boil, insuring the same temperature, and are boiled for a fairly uniform length of time. Few, however, consider the importance of using a definite amount of acid. It seems to be a prevalent idea that the amount of silica dissolved by the acid solution is proportional to the amount of SiO_2 in the sample. When a small bulk of acid is used, this is certainly not the case. Experiments prove clearly that when a small amount of SiO_2 is present, the amount dissolved is proportional to the quantity of acid solution present and not to the amount of SiO_2 in the sample.

RECOMMENDED PROCEDURE FOR SILICA (HAWLEY'S METHOD)

A modification of the peroxide method, as used for routine work, is as follows: Weigh 0.5 gram of pulp into a 30 ml. nickel crucible and add one scoopful (about 4 grams) of flux composed of equal parts of sodium peroxide and sodium hydroxide. Mix the pulp and flux, and if the sample is known to contain over 50% of SiO_2 put on a cover to prevent loss. Fuse at a low temperature, beginning much below redness and increasing very slowly until a dull red is reached.

When the fusions are made as described the nickel crucibles can be used from 20 to 40 times, but if the temperature is too high, or if there is too much sodium peroxide in the flux, they will burn out much quicker.

Remove the crucibles and partly cool; place in 4-in. casseroles, and cover the crucibles with 2-in. watch glasses so placed that a slight opening is left on one side. Through this opening squirt in 2 or 3 ml. of warm distilled water from a wash bottle. This should start a vigorous reaction between the water and the flux. As soon as the action has somewhat diminished add 3 or 4 ml. more water and continue to do this until the fused mass is disintegrated. Toward the end the water should be added with enough force to thoroughly stir the contents. If the crucible gets too cold or the water is not hot enough, the action may cease before the melt is loosened from the crucible; and if too hot the contents may boil over. With a little practice the right conditions are readily found. As soon as the action ceases and the crucible is a little over half full, rinse off the watch glass and from a large burette add about 10 ml. of 60% HCl in small portions so as to avoid too violent reaction; then add 90% HCl until it is in excess. The crucible should now be about full and everything in solution except possibly a little gelatinous silica.

With the fingers or platinum-tipped tongs, remove the crucible, rinse, and place the casserole on the hot plate to evaporate. No harm is done if it boils gently at first. When about half evaporated, place the casserole on an iron or aluminum ring so made that the bottom of the casserole is kept about one-quarter inch above the hot plate. These rings are very beneficial in preventing spitting. When the residue has become dry, cover with a watch glass and bake at about 125° C. for 30 minutes; remove and when cool add 15 ml. of 60% HCl and turn about so as to moisten all parts of the residue. Allow to

stand a short time and then put on the hot plate, and with cover still on, boil for 3 min. Remove and allow to cool, rinse the sides down with the minimum amount of warm distilled water, and swirl around to loosen any crust still adhering to the sides. The NaCl does not all dissolve, but will readily do so in the wash water.

It is very necessary that the casserole should not be heated after rinsing down the sides with water. After standing a few minutes, transfer the contents to a filter and wash twice with warm water; then once with hot dilute HCl and add a little to the casserole. Rub the sides and bottom of the casserole to loosen any adhering SiO_2 and rinse into the filter. This SiO_2 is ground rather fine by the rubbing and has a tendency to clog the filter, hence it is better to add this after the main portion has been partly washed. Wash the filter twice again with water, place in a crucible, partly dry, and ignite strongly for ten minutes. Weigh the SiO_2 as soon as cool, for it is hygroscopic. A correction is now made for the SiO_2 lost in solution, which under these conditions will amount to about 0.4%. A deduction is made for impurities in the SiO_2 and the SiO_2 from the flux. These gains about balance the solubility loss. Occasional tests should be made to check these losses and gains.

Silicon in Presence of High or Low Chromium in Steel.—See A. S. T. M. Methods of Chemical Analysis of Metals, E 30–36 T, page 27, 1936 ed.

ANALYSIS OF FERRO SILICON AND REFINED SILICON [17]

DETERMINATION OF SILICON

This determination is based on decomposition of the sample by fusion with sodium peroxide in a pure iron crucible, acidification with hydrochloric acid, and dehydration and determination of the silica by the usual procedures. While the method is simple in theory, it requires more than ordinary care and attention to details if accurate results are to be obtained. A majority of the chances for error due to careless manipulation are of a character which result in loss of silica, consequently it is very usual for low silicon results to be obtained.

Into a 30 ml. iron crucible there is weighed 0.4672 gram of the sample of *ferro-silicon* or *refined silicon* which has been ground to at least 200-mesh in an agate mortar. The fine pulverization of the sample is necessary in order to secure complete decomposition by the subsequent fusion. The crucibles are stamped from No. 20 gauge (0.038″ thickness) "Armco" iron and can be purchased from the Consolidated Manufacturing Company, Dayton, Ohio. This iron (called "Ingot Iron") contains only a trace of silicon and the crucibles made from it are more satisfactory for this particular purpose than nickel

[17] Contributed by Thos. R. Cunningham.

crucibles (which always contain some silicon) and cost only a fraction as much. Approximately 8 grams of dry sodium peroxide are added, the contents are mixed thoroughly with a small iron or nickel rod, and the mixture is covered with a layer of about 2 grams additional sodium peroxide.

The contents of the crucible are carefully fused over the flame of a laboratory burner. Instead of a gas flame, an electric crucible furnace or other source of heat may be employed, but the former is preferable. The fusion is best accomplished by holding the crucible with a pair of tongs and slowly revolving it around the *outer edge of the flame* until the contents have melted down quietly, care being taken not to raise the temperature so rapidly as to cause spattering. When the fusion is molten, a slight rotary motion is imparted to the crucible to stir up any unattacked particles of alloy on the bottom or sides, the crucible and contents being maintained at a low red head. Just before completion of the fusion, which only requires three or four minutes, the temperature is increased to bright redness for a minute. If these directions are followed carefully, a very quiet fusion without any spattering will result, and complete decomposition will be obtained. In event of a violent reaction, due usually to too rapid heating, use of insufficient sodium peroxide, or to lack of thorough mixing, appreciable loss will occur and the work should be repeated.

When the tightly covered crucible has cooled a sufficiently long time for the fusion to solidify, but before it has reached room temperature, it is tapped on an iron plate several times to loosen the fused mass from the crucible in a solid cake. When the melt has cooled, it is transferred to a large (275 ml.) covered platinum dish, to which there is cautiously added 50 ml. of cold water. As soon as the reaction is over the dish and its contents are allowed to cool somewhat, 10 ml. of sulfurous acid and approximately 50 ml. of hydrochloric acid (more is used if necessary) are introduced which should render the liquid acid and result in the solution of everything except a few particles of magnetic iron oxide which will dissolve during the subsequent evaporation. The solution is evaporated to dryness on a sand or water bath and heated for about 30 minutes at a temperature approximating but not exceeding 110° C. More prolonged heating, or heating at higher temperatures, is disadvantageous since it renders the iron oxide more insoluble. The use of a platinum rather than a porcelain dish is a matter of considerable practical importance. It is very difficult to remove all silica from a porcelain dish whereas this is easily accomplished with platinum. On the other hand, alkaline chlorides attack a porcelain dish after a few evaporations, when the glaze has worn off, introducing an error which leads to high results. For these reasons platinum, when available, should always be employed.

After having allowed the dish to cool, 20 ml. of hydrochloric acid (sp.gr. 1.19) are introduced and heat is applied for about 5 minutes, any hard lumps being broken up with a glass rod. Approximately 150 ml. of water are then added and the solution is heated just sufficiently long to dissolve most of the sodium chloride, when it is filtered on an 11 cm. ashless paper and washed 10 or 12 times with hot 2% hydrochloric acid and then thoroughly with hot water. The filtrate and washings are reserved. Dehydrated silica is appreciably soluble in hydrochloric acid of all strengths and also in solutions of sodium chloride. The important factors affecting this solubility are the strength and volume of acid used its temperature, and the length of time the silica is exposed

to the action of the acid and sodium chloride solution. The most important of these factors is the volume of acid employed. Adherence to the conditions described will result in a minimum of silica being dissolved. When the silica has been washed thoroughly it is reserved for further treatment.

To the combined filtrate and washings from the silica, there are added 60 ml. of sulfuric acid (sp.gr. 1.84) and the solution is evaporated in a porcelain dish or casserole until dense fumes of sulfur trioxide are freely evolved. Use of porcelain at this point is permissible because the glaze is not appreciably attacked under these conditions and silica which has been dehydrated by sulfuric acid is gelatinous and can be easily removed from a porcelain surface. After having allowed the residue of ferric sulfate, sodium sulfate, etc. to cool, 250 ml. of water are added and the solution is boiled until the sulfates are in solution, when it is immediately filtered on an 11 cm. ashless paper and the silica washed 10 to 12 times with cold 1% hydrochloric acid and then thoroughly with hot water. The small amount of silica which passes into the filtrate may be neglected.

The paper and silica from the second dehydration are placed in a large covered crucible and the paper is burned. The paper containing the silica from the first dehydration is then added and ignited very carefully at a very low red heat until the carbon has burned. Great care should be exercised in igniting the paper as the current of air produced by a burning filter paper is sufficient to carry finely divided silica out of the crucible. Carelessness at this point may result in loss of several per cent of silicon. When the carbon of the filter paper has burned completely, the crucible and its contents are ignited to constant weight with a blast lamp or in an electric muffle furnace at from 1100° to 1150° C.

After the crucible has been cooled in a desiccator and weighed, the precipitate is moistened with water, 2–3 drops of sulfuric acid (sp.gr. 1.84) and from 5 to 10 ml. of pure hydrofluoric acid (48%) are added and the solution is evaporated on a sand bath until the acids have been expelled, when the crucible is again ignited for a few minutes and weighed. The difference between the two weights, less the " blank " on the sodium peroxide, multiplied by 100, gives the percentage of silicon.

A factor weight (0.4672 gram) of the 100-mesh sample of 15% ferro-silicon is fused with approximately 10 grams of sodium peroxide in an Armco iron crucible. The solution is acidulated with 80 ml. of sulfuric acid (1:1) and evaporated to fumes of sulfur trioxide.

Sodium peroxide usually contains only very small amounts of silica, but as a precaution a " blank " should be run on each new can that is employed. This is done by dissolving 10 grams of the reagent in water in a platinum dish, acidifying the solution with hydrochloric acid, evaporating to dryness, etc., as previously described. The amount of silica found in this way is usually negligible when compared to the errors to which the method is subject.

CONDUCTIVITY METHOD FOR DETERMINING SILICON IN MAGNETIC SHEET STEEL [18]

The desirability for a more dependable and quicker method for determining the percentage of silicon in magnetic sheet steel has been recognized for several years.

Inclusion of silicon in magnetic sheet steel affects both the physical and magnetic qualities of the steel; for instance, the specific gravity of the steel will change with the silicon content and this must be considered when computing the core losses; and steel containing over four per cent silicon is so brittle that it is unfit for use in the rotating members of electric machines. Mr. W. E. Ruder in "The Effect of Chemical Composition Upon the Magnetic Properties of Steels," General Electric Review, pp. 197 to 203, March, 1915, observes the following changes attributible to silicon:

1st: It prevents the formation of hardening carbon, even with comparatively quick cooling.

2d: It cleanses the metal of harmful oxides and dissolved gases.

3d: It produces a larger grain structure in the metal.

4th: It increases the resistivity of the metal from 12 to about 60 or 70 microhms per cm. cube depending upon the contents.

The American Society for Testing Materials (Specifications A-34-23T) states that 2% silicon steel should have an electric resistivity of 2.6 ohms per meter gram.

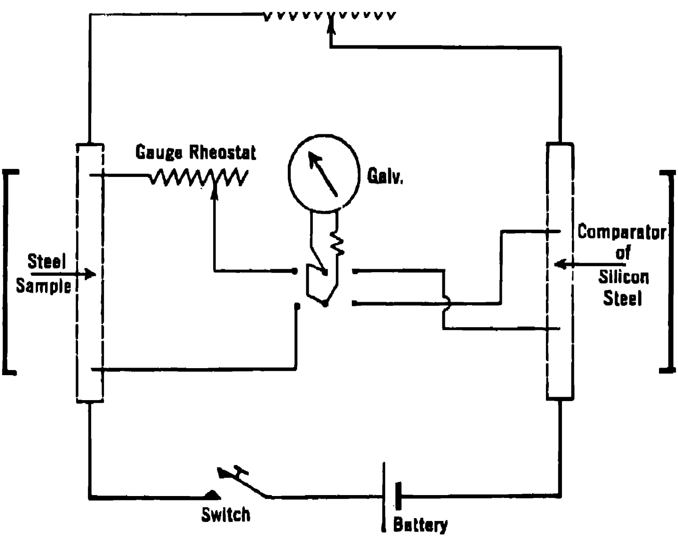


FIG. 97.

This 2.6 ohms per meter gram = 34.7 microhm cm.^{3}

From the curve 2% silicon steel = 36.0 microhm cm.^{3}, which is within 4% of the values set by the A. S. T. M. at this point.

[18] P. L. Stapleton, General Electric Company.

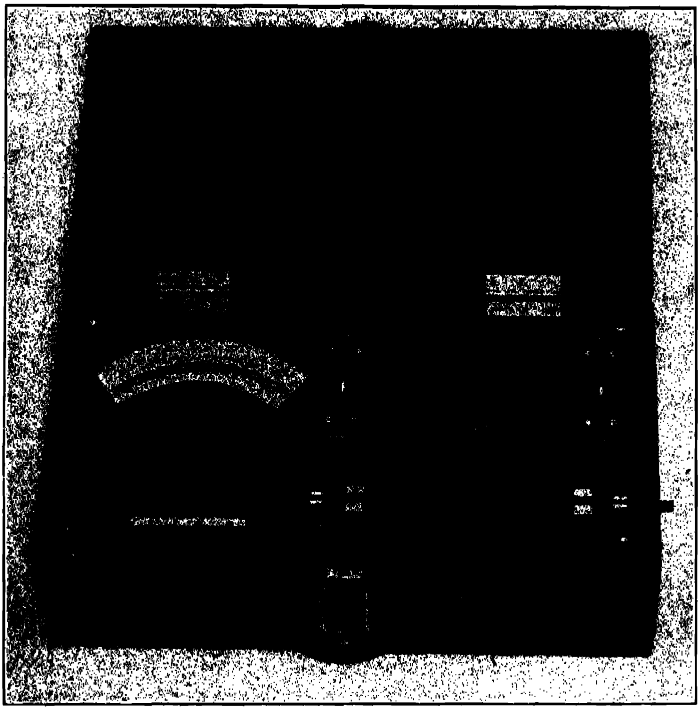


FIG. 98.

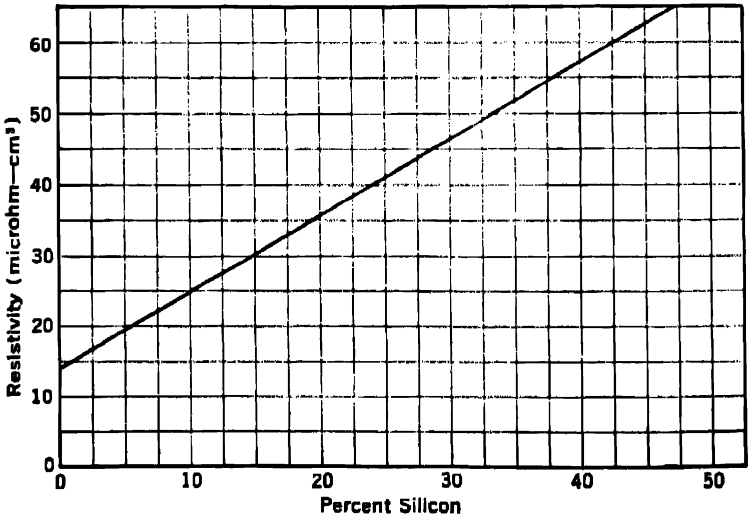


FIG. 99.

Electrolytic iron has a resistivity of approximately 10 microhms per cm.³ but it was found that commercial grades of magnetic sheet containing practically no silicon and obtained from several different sources had a resistivity of 14 or 15 microhms per cm.³; it will be observed that this is the starting point of the curve.

With this data it has been possible to construct a very dependable instrument for making silicon determinations; the wiring scheme for the instrument is presented in Fig. 97.

Figure 98 shows the instrument with the sample of steel inserted for testing. Fig. 99 gives resistance as of function of percent of silicon.

There are two features incorporated in the instrument which deserve special mention: the first is the " Comparator " which is made of silicon steel (about 2.5% silicon) and is protected from corrosion by a coating of G. E. No. 880 protective paint baked on at a temperature of 100 degrees centigrade.

Since this " Comparator " is used in controlling the current and as it is constructed of the same material as the samples under test, it has the effect of compensating the instrument for temperature changes. Samples have been tested over a wide range of temperature and no appreciable errors have been noted in the indications.

The second feature is the " Graduated Rheostat " which makes it possible, by manual setting of the dial, to test steel of various thicknesses ranging from .013″ to .026″ and accurately to 1/5 of a mil. This eliminates entirely all computations and multiplying factors, and reduces the testing of the steel to a purely manual operation.

Instructions for operating the instrument are as follows:

1st. Insert the strip of steel in the current clips and tighten the potential contact points against it.

2d. Adjust the " Graduated Rheostat " to the thickness of the steel to be measured.

3d. Close switch at right of instrument; then close switch at left to position marked " Comp.," and adjust galvanometer pointer to the red line on the scale by turning the lower rheostat.

4th. Close switch at left to position marked " Samp.," and read the percentage of silicon directly from the position of the galvanometer pointer.

ANALYSIS OF SILICON CARBIDE [19]

I

UMPIRE METHOD

A. Decomposition of Sample.—The silicon carbide, powdered to pass through a 150 mesh screen, is dried at 110° C. for one hour to remove hygroscopic water. All analyses are made on the dried sample.

Weigh out approximately .5000 gram of sample and transfer to a platinum crucible of about 30 ml. capacity, somewhat larger if available. Mix thor-

[19] Methods used by the Norton Co., Worcester, Mass., through the Courtesy of M. O. Lamar.

oughly with 5 grams of the purest sodium carbonate, anhydrous, and place over a small flame of a Bunsen burner. Start with the bottom of the crucible at dull red heat and very slowly increase the temperature. It is important that this operation not be hurried for violent spattering will ensue and particles of SiC will be carried onto the cover and remain unattacked. As soon as the reaction of decomposition starts, ascertained by carefully lifting the cover for an instant, maintain that temperature for half an hour or more. The mass should be semipasty and not too fluid. Finally, with great care increase the temperature to full heat of the burner and continue the fusion for half an hour. If these conditions are rigidly adhered to, it is unnecessary to add any sodium or potassium nitrate to the fusion. Keep the flame of the burner oxidizing and do not envelop the crucible with a large semi-reducing flame. The platinum crucible is not attacked more than in an ordinary sodium carbonate fusion of a rock or clay.

B. Total Silica.—When the fusion is complete transfer the contents of the crucible to a 400 ml. dish, preferably of platinum, cover with a watch glass, add 150 ml. of hot water and then 35 ml. of 1 : 1 hydrochloric acid. When all effervescence is over, rinse off the watch glass into the dish, clean the crucible and cover in a similar manner and evaporate the contents of the dish on the steam bath to complete dryness. Cool, drench the residue with 10 ml. of concentrated HCl, let stand five minutes, add 100 ml. of hot water, digest 10 minutes on the steam bath, filter off the silica, and wash free from chlorides with warm water. Evaporate the filtrate to dryness in the same dish, heat to 100° to 120° C. for one hour and repeat the silica filtration and washing.

Ignite the two papers in a platinum crucible, blast to constant weight and correct the silica for impurities with hydrofluoric acid and sulfuric acid according to the standard procedure.

The residue in the crucible is fused with a pinch of bisulfate, dissolved in water and added to the filtrate from the second silica. Heat the filtrate to 80–90° C. and gas thoroughly with H_2S. Let stand one-half hour at least, filter off the platinum sulfide, and wash with acidulated H_2S water. Boil out the H_2S from the filtrate and oxidize the iron by the addition of bromine water to a distinct yellow color. Finally boil out the bromine and bring the volume of the solution to 150 ml. by evaporation. The solution is now ready for the determination of iron oxide, alumina, titania, etc.

C. Total Ammonia Precipitate.—Add a few drops of methyl red to the boiling hot solution and then dilute, carbonate-free, freshly prepared or redistilled ammonia until the indicator changes to yellow. Boil one or two minutes and filter, washing the precipitate with hot 2% neutral ammonium chloride solution. Dissolve the precipitate in a few ml. of hot dilute acid, wash the paper thoroughly and reprecipitate with the same precautions as above. Reserve the precipitate. Combine the two filtrates, make slightly acid, and concentrate to a volume of 100 ml. Make faintly ammoniacal, add bromine water and digest 1–2 hours on the steam bath, keeping the solution ammoniacal. Filter off any manganese precipitate which may have separated, wash and dissolve in dilute HNO_3 containing a pinch of sulfite. (Note: If desired, determine Mn by any acceptable method. The amount is so small that color methods suffice.)

D. Lime and Magnesia.—Determine lime and magnesia by the usual methods, making a double precipitation in each case. Allow the first precipitate of calcium oxalate and magnesium ammonium phosphate to stand over night. The second precipitate need stand only about six hours, though longer does no harm.

E. Separation of Fe_2O_3, TiO_2, etc., from Al_2O_3.—(*a*) The weighed total ammonia precipitate is fused with a small amount of pyrosulfate and taken up in 2% sulfuric acid. Gas with H_2S to remove traces of Pt and filter if any appears. Add one gram of tartaric acid, pass in more H_2S, make ammoniacal and continue gassing for 5–10 minutes. Let stand warm for one-half hour and filter off FeS, washing with 2% NH_4Cl solution containing some colorless ammonium sulfide. Reserve the filtrate. Dissolve the precipitate in hot 1 : 3 hydrochloric containing a pinch of potassium chlorate. Wash the paper thoroughly and boil the chlorine out of the filtrate. Precipitate the iron with ammonia from the boiling hot solution, wash the precipitate with hot 2% ammonium chloride solution and weigh as Fe_2O_3.

(*b*) The filtrate from the H_2S precipitation is made acid with H_2SO_4 and boiled down to a small volume. Titania can be determined either colorimetrically with H_2O_2 or precipitated along with whatever ZrO_2 that may be present by means of " Cupferron " from an ice-cold solution containing 10% by volume of sulfuric acid.

From the sum of the $Al_2O_3+Fe_2O_3+TiO_2$ precipitate Al_2O_3 is found by difference. This ignores the possible presence of several other elements (P_2O_5, for example) but the minute amounts present do not usually warrant separate determinations. Calculate the oxides to metals.

F. Free Carbon.—This determination is the least satisfactory of all, since it is very difficult to burn out free carbon without some oxidation of the silicon carbide. Best results are obtained when a weighed, dry sample is ignited in a boat in an inclined tube furnace at 950° C. for 15 minutes. The loss in weight is assumed to be carbon. No better results are obtained if the CO_2 is weighed after absorption in ascarite or other such materials.

G. Total Carbon.—Weigh out .2500 of the dry sample, mix thoroughly by shaking in a small weighing bottle with 1.50 grams of the very best Pb_3O_4. Transfer to a combustion boat lined with RR Alundum, rinse out the bottle with RR Alundum and pour on top of the sample. Cover with more Alundum if necessary. Burn the sample at 1000–1100° in a combustion furnace with oxygen, absorbing the CO_2 exactly as for steel analyses. All Pb_3O_4 contains some carbonaceous matter; therefore run several careful " blank " determinations using exactly the same conditions. If there are indications that all the sample did not burn, crush the fusion in a clean mortar, add more Pb_3O_4 and reburn the sample. This condition sometimes arises.

Calculations.—From the percentage of total carbon, subtract " free carbon," obtaining the per cent of combined carbon. Calculate this to SiC which gives the percentage of silicon carbide in the sample. Next calculate the SiO_2 equivalent of the SiC and subtract the result from the total silica found. The difference is " total free silica." From the total summation of the analysis subtract 100.00%; the difference is excess oxygen. Excess O_2 times the factor SiO_2/O_2 gives the amount of silica equivalent to the excess oxygen. Subtract this figure from the " total silica; the difference is the *free* silica present. The

"total free silica" minus the "free silica" gives the SiO_2 derived from the *free silicon present.* Calculate to Si by the factor Si/SiO_2.

Iron, aluminum, and titanium are reported as metals, for it is a reasonable assumption that they are present in the lowest state of oxidation. Calcium and magnesium are reported as their respective oxides.

It is apparent that the summation of the analysis should be exactly 100.00% since some of the constituents (SiO_2 and Si, for example) are calculated on the basis of that assumption.

THE ACETIC ANHYDRIDE METHOD FOR DETERMINING SILICA IN CEMENT AND CLINKER

Mr. R. M. Willson, the chief chemist of the Southwestern Portland Cement Company at Victorville, Calif., has developed the following method of procedure for the determination of silica in cement and clinker. This method is a modification of the glacial acetic acid method.

Weigh half a gram of sample in 150 ml.-pyrex beaker. Rotate beaker while adding to it a mixture of 5.5 ml. of acetic anhydride, and 4.5 ml. of distilled water. Place on hot plate and rotate until violent action ceases. Remove the beaker to an asbestos pad which was previously heated and placed by the side of the hot plate. When action has ceased and the solution assumes a uniform reddish color, add a very small amount of 1 : 1 hydrochloric acid (not more than 5 ml.). Heat to clear yellow. Add 10 ml. of distilled water, and filter silica. Proceed identically as with standard method of analysis, only use a little more caution to be sure the solution is ammoniacal on the first precipitation of the R_2O_3.

The above outlined method of procedure has been used by the Southwestern Portland Cement Company at Victorville for more than ten years. It is characterized by speed, accuracy and simplicity. The time factor is always an important consideration in an industrial laboratory. It is obvious this method is rapid since the time and trouble of evaporation is entirely eliminated. Recently perchloric acid has been recommended as a rapid method for the dehydration of silica in cement or clinker. Acetic anhydride will accomplish the same purpose in far less time, and also do away with the danger of explosion which occasionally occurs when perchloric acid is used. The total time of dissolving the sample and filtering the silica should not take longer than five minutes. Compare this with the two or more hours for double evaporation in a casserole or the fifteen to twenty minutes required in the perchloric acid method.

If reasonable precaution is observed, the silica obtained by the acetic anhydride method is purer than when hydrochloric acid is used. Check results of silicas obtained by both methods, prove that the acetic anhydride dehydration of silica is equivalent to a double evaporation of the standard hydrochloric acid method. The following samples of cement were sent to an outside labora-

tory for analysis and will serve to illustrate the accuracy of the method described. This laboratory dehydrated the silica by both a single and double evaporation in a casserole using 1 : 1 hydrochloric acid as a solvent. In the single evaporation, .3% was deducted from the R_2O_3 and added to the SiO_2. These samples were also analyzed at Victorville by acetic anhydride. No correction was made on the silica.

Sample No. 1

	Single evap.	Double evap.	Acetic anhydride
SiO_2	19.10	19.40	19.40
Al_2O_3	6.40	5.90	6.60
Fe_2O_3	3.30	3.20	3.10
CaO	64.32	64.10	64.30
MgO	2.40	2.43	2.32
SO_3	2.32	2.36	2.20
Ignition loss	1.70	1.55	1.50

Sample No. 2

	Single evap.	Double evap.	Acetic anhydride
SiO_2	19.40	19.68	19.80
Al_2O_3	6.20	5.95	6.02
Fe_2O_3	3.20	3.05	3.18
CaO	64.30	64.70	64.50
MgO	2.55	2.64	2.45
SO_3	1.97	1.98	2.00
Ignition Loss	1.51	1.70	1.75

Sample No. 3

	Single evap.	Double evap.	Acetic anhydride
SiO_2	19.35	19.45	19.40
Al_2O_3	6.23	5.95	6.12
Fe_2O_3	3.05	3.05	3.08
CaO	65.00	64.90	65.10
MgO	2.57	2.64	2.57
SO_3	1.58	1.60	1.60
Ignition Loss	1.68	1.68	1.49

It will be noticed in all of these samples that the silica obtained by the acetic anhydride method is equivalent to a double evaporation and that there is no apparent interference in the subsequent separation of the other components in the cement.

Written by Carroll B. Core, assistant chief chemist, at the request of Mr. R. M. Willson, Chief Chemist of the Southwestern Portland Cement Co., Victorville, Calif.

SILVER [1]

Ag, *at.wt.* 107.88; *sp.gr.* 10.50-10.57; *m.p.* 960.5° C.; *b.p. about* 1950° C.; *oxides*, Ag_2O, Ag_4O, Ag_2O_2

Silver occurs native as metallic silver, but more commonly in combination as silver glance or argentite, Ag_2S; as antimonide, arsenide, bismuthide, bromide, chloride, iodide, selenide, sulfide, telluride, and in thio salts. It is found associated with sulfide of lead, with native gold and copper, with antimony, mercury, bismuth and platinum. Among the more important minerals are: —native silver, argentite, hessite, proustite, pyrargyrite, cerargyrite (horn silver, AgCl). Traces of silver occur in sea water.

DETECTION

A trace of silver in most substances is detected with greatest certainty by furnace assay methods.

The wet method of detection of silver most commonly practiced, depends upon observation of the properties of the precipitate formed by the addition of a not excessive amount of alkali chloride to a cold nitric or sulfuric acid solution of the substance undergoing examination. One-tenth milligram of silver precipitated as silver chloride in a cold 200-ml. acid solution gives a very perceptible opalescence to the liquid.

Silver chloride is white when freshly precipitated, tinted pink when palladium is present; in colorless liquids on exposure to light turns brown, violet, blue or black. By agitation, heating or long standing the precipitate becomes coagulated or granular and in such a state is retained by an ordinary filter. The presence of some forms of organic matter prevents coagulation.

Silver chloride is dissolved by concentrated hydrochloric acid; raising the temperature of the acid assists the action. It is dissolved by sodium thiosulfate, alkali cyanides, mercuric nitrate, and alkali chlorides.

From mercurous chloride, silver chloride, except when constituting a small proportion of the precipitate, is distinguished by its solubility without decom-

[1] Silver has been known from prehistoric times and has been employed as a standard of value in coins many centuries before the Christian era and still continues in the currency of all civilized countries of the World. Copper is now added to increase the durability of the coins, the United States coinage containing 10% of copper, British coins 7.5% copper. The element is used in silver-plating, making of mirrors, table silverware, and jewelry and ornaments. The nitrate is used in cauterizing wounds, the chloride and bromide salts are employed in photography.

position in ammonia. Precipitation from its ammoniacal solution is accomplished by acidifying. Lead chloride, precipitable also by hydrochloric acid, is not flocculent, does not coagulate, but dissolves quite freely by heating. Addition of hydrochloric acid to a solution of silicon, tellurium, thallium, tungsten or molybdenum may produce a precipitate, in each case, easily distinguishable from that of silver chloride, but may mask traces of the salt.

Silver, in a cold solution containing free nitric acid, only a small amount of colored salts and no mercury, may be detected through the formation of a white precipitate, similar in appearance to silver chloride, by addition of a slight excess of an alkali thiocyanate.

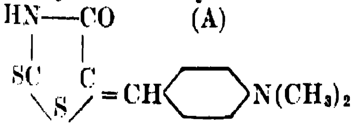
When a solution of silver salt is added to a mixture of 20 ml. ammonium salicylate (20 grams. salicylic acid neutralized with ammonia, a slight excess added and the whole made up to 1000 ml.) and 20 ml. of a 5% solution of ammonium persulfate added, an intense brown color is produced, which will detect the presence of a 0.01 milligram of silver. Lead does not affect the test.

When it appears that the chloride or thiocyanate test for silver is not positive on account of the presence of other precipitable elements, the precipitate, after it settles, is filtered through the finest quality of paper, and the mixture of the ash of the incinerated filter with dry potassium carbonate heated on charcoal with a mouth blowpipe. If silver is present and not associated with a large amount of palladium, there will be found on the charcoal pellicles of the color characteristic of silver, which have no white or yellow sublimate when melted in the oxidizing flame of the blowpipe. The pink palladium salts of silver precipitated by a chloride or thiocyanate before the blowpipe produces metal which is dull in appearance and not readily melted.

NOTES.—Silver may be recognized in a solution of concentration 1 to 240,000 by the reduction of its salts with alkaline formaldehyde. Whitby's method of detection and estimation of small amounts of silver depends upon the formation of a yellow color through addition of sucrose and sodium hydrate. Ammonium hydrate interferes, but bismuth, cadmium, copper, mercury of either valence, lead or zinc, in amounts equal to that of the silver, do not. Maletesta and DeNola add to the solution to be tested a few drops of a solution of nitrate of chromium and then potassium hydrate to alkalinity. A brownish turbidity or black precipitate of silver oxide forms. The limit of sensitiveness is 0.5 milligram in 100 ml.

F. Feigl[2] has described a new and very delicate test for silver with p-dimethylaminobenzylidene-rhodanine as a reagent. According to Feigl, this

(A)



reagent gives in weakly acid, neutral and ammoniacal solutions, a flocculent red precipitate with silver. In 5 ml. of a weakly acid solution, one part of silver in 5,000,000 of solvent could be detected. In working with 10 ml. of solution, to which 0.5 ml. of 4 N nitric acid and 0.3 ml. of a saturated solution of the rhodanine[3] in alcohol were added, the same sensitivity was found.[4] A solution with 1 mg. of silver in a liter produces a distinct reddish brown color (10 ml. of solution, conditions

[2] F. Feigl, Z. anal. Chem., 74, 380 (1928).

[3] The reagent is prepared according to the procedure given by Feigl. Instead of using a 0.03% solution of the rhodanine in acetone as described by Feigl, a saturated solution in alcohol (about 0.02%) may be taken.

[4] I. M. Kolthoff, J. Am. Chem. Soc., 52, 2222 (1930).

as above); with 0.5 mg. of silver per liter a weakly reddish color was noticed; with 0.2 mg. per liter the solution showed a very weak pink color after ten minutes' standing, distinctly different from the blank, which was slightly yellow. In ammoniacal solution (10 ml. of solution + 1 ml. of 6 N ammonia and 0.1 ml. of indicator) the color in the presence of silver is reddish-brown and in very dilute solutions orange-brown. The sensitivity in this case is about 2 mg. of silver in a liter.

In acid medium the reagent is so sensitive toward silver that it even cannot be used as an indicator for the titration of iodide with silver solution. A weakly acid solution of 0.01 N potassium iodide to which some reagent had been added gave a dark red precipitate after addition of a few drops of 0.01 N silver nitrate. Even the silver in the complex potassium silver cyanide reacts with the rhodanine.

Feigl's reagent may also be applied to the estimation of traces of silver in water by colorimetric technique. This determination is of interest because of the development of the electrolytic silver method for sterilizing water for swimming pools, etc. (Kathadyn method). Soft glass vessels should not be used; Jena glass is suitable and fused silica is best. Silver ion is adsorbed on the surface of soft glass.[5]

Dithizone may be used to detect silver or to determine it colorimetrically in the absence of Cu, Hg, Au, Pd and Pt^{II}. The acidified solution of the silver is extracted with dithizone in CCl_4 (See Lead Chapter for general technique). The silver salt of the reagent is yellow.[6]

ESTIMATION

Silver is determined in copper, lead, silver, sulfur or other ores, in copper and lead furnace by-products, and in lead by furnace assay methods, in which a preliminary acid treatment of the sample is rarely employed; in native copper ore, in copper, copper alloys, gold, gold alloys and in the slime from the electrolytic refining of copper or lead by furnace methods, in which a preliminary acid treatment of the sample is employed, in silver alloys by volumetric or gravimetric methods; in mercury by a gravimetric method; in cyanide mill solution or solutions containing much organic matter by furnace process on the residue obtained by evaporation or precipitation; in silver plating electrolyte by electrolysis.

Solubility.—Nitric acid, dilute or concentrated, attacks silver rapidly when hot. The presence of a soluble chloride, iodide or bromide in the solvent or substance will retard and may prevent solution. Unless oxidizing agents are present, dilute sulfuric acid has practically no action on massive silver, but

[5] I. C. Schoonover, J. Research Nat. Bur. Standards, 15, 377 (1935).
[6] Fischer, Leopoldi and von Uslar, Z. anal. Chem., 101, 1 (1935).

hot, concentrated acid commences to be an active solvent at a concentration of 75% H_2SO_4. Hydrochloric acid attacks silver superficially. The action of alkali hydrates or carbonates in solution is inappreciable; in a state of fusion, slight.

Furnace Assay Methods.—These will be described in the chapter devoted to that subject.

In procedures where HCl has been employed and precautions have not been taken for obtaining silver, practically all of this will remain with the silica residue, generally reduced to metallic form. In presence of silver the dehydration of silica must be done with sulfuric acid and the silver then extracted as sulfate, and precipitated from acid solution as sulfide.

Silver bearing ores are best extracted with nitric acid followed by fusion of the acid residue.

SEPARATIONS

Silver is quantitatively precipitated as chloride in acid solution. Interferences that require separation, if present, are lead, uni-valent mercury, copper and thallium. Bismuth and antimony form precipitates of oxychlorides with sufficient dilution. Cyanides and thiosulfates dissolve the AgCl, and must be absent. Oxidation in the preliminary treatment prevents the co-precipitation of Hg, Cu and Tl. $PbCl_2$ is soluble in hot water while AgCl is but slightly soluble. In 0.01 N chloride solutions the solubility of AgCl at 25° C. is 0.002 mg. per liter. Ag_2S is quantitatively precipitated by H_2S in acid or alkaline solution, facts affording methods of separation of Ag from the $(NH_4)_2S\cdot$, $(NH_4)_2CO_3$ groups and from As, Sb and Sn, respectively

GRAVIMETRIC METHODS FOR THE DETERMINATION OF SILVER

PRECIPITATION AS SILVER CHLORIDE [7]

Introductory.—Although silver might be determined as an iodide or bromide, the fact that these halides are more sensitive to light than the chloride, and decompose more readily, with liberation of the halide and the formation of subhalides, has led to the precipitation of silver as the chloride.

Reaction.—$AgNO_3+HCl=HNO_3+AgCl$.

[7] Contributed by Wilfred W. Scott.

Reagents. ***Hydrochloric Acid.***—One volume of concentrated HCl (sp.gr. 1.19) diluted with five volumes of water (sp.gr. of dilute HCl 1.035); 1 ml. contains 0.074 g. of HCl, equivalent to 0.219 g. of Ag.

Nitric Acid.—One volume of concentrated HNO_3 diluted with 1.6 volumes of water (sp.gr. of acid is 1.2); 1 ml. contains 0.38 g. of HNO_3, which would dissolve 0.64 g. of Ag.

1. **Preparation of the Sample. Solution.** ***Silver Alloys.***—Place 0.5–1.0 gram of the alloy in an Erlenmeyer flask and add 5 ml. of the dilute nitric acid. Heat gently until the alloy is dissolved and the brown fumes are expelled. The solution is now diluted to about 100 ml. and the silver precipitated as stated below.

Soluble Silver Salts.—The salt is weighed into a weighing bottle; 1.0–2.0 grams are sufficient for a determination. The solution is now diluted to about 100 ml. and the silver precipitated as stated below.

The Halides of Silver.—These are best brought into solution by fusion with about six times the weight of the sample of sodium carbonate. This converts the silver into the carbonate and the halide combines with sodium and is dissolved out in water. The silver carbonate is washed free of the halide and then dissolved out in dilute nitric acid.

Ores of Silver.—These may be brought into solution by digestion with nitric acid, the residue remaining is treated as stated above under halides of silver. Unless the ore is very high in silver, it is preferable to make the analysis by Fire Assay.

2. **Precipitation of Silver Chloride.**—Heat the solution to boiling and add from a burette, drop by drop, 5 ml. of dilute hydrochloric acid. This is sufficient to precipitate over 1 gram of silver. The excess of acid is desired as the chloride is less soluble in free hydrochloric acid.

NOTE.—The chloride is soluble in concentrated hydrochloric acid, hence a large excess is undesirable. Shaking or vigorously stirring the mixture will clear a cloudy solution. This is necessary to coagulate the silver chloride, as the fine suspended silver chloride will pass through the filter paper.

3. **Filtration: (Procedure if Filter Paper is Used).**—Decant the clear solution into the filter. Test the filtrate with a drop of dilute HCl to make sure all the silver is precipitated. Now wash two or three times by decantation, using hot water containing 1 ml. of HNO_3 per 100 ml. of distilled water. Transfer the silver salt to the filter and continue washing until free from chlorides. Six to eight additional washings should be sufficient.

4. *Dry* the filter and silver salt in the oven at 100–110° C.

5. *Remove* as much of the silver chloride as possible from the paper, placing the salt on a glazed sheet of paper, covering it with a watch glass.

6. *Ignite* the filter in a crucible (whose weight has been ascertained), then add to the ash a drop of nitric acid and a drop of hydrochloric acid. Heat gently to expel the acids. (Handle the crucible with tongs. Do not place on the table.)

7. *Transfer* the chloride from the glazed paper to the crucible and heat gently until the salt just begins to fuse on the sides of the crucible.

8. *Cool* in a desiccator for fifteen to twenty minutes.

9. *Weigh* as AgCl, making an allowance for the weight of the crucible. $AgCl \times 0.7527$ gives the weight of Ag in the salt.

10. Calculate the per cent silver from the weight of sample taken.

3*a*. **Procedure if a Gooch Crucible is Used.**—Prepare a Gooch crucible with a fairly thick pad of asbestos fibre (1/8 in. thick). Wash once with alcohol and dry to constant weight at 110° C. Keep a record of the weight.

4*a*. *Wash* the precipitate by decantation, pouring the washings through the Gooch, with application of suction. Transfer the chloride to the crucible and wash free of chlorides.

5*a*. *Finally* wash once with alcohol and dry at 110° C. to constant weight.

6*a*. *Calculate* the percentage of silver as directed in the first method.

NOTES.—*Solubility* of the silver halides. Milligrams of salt per 100 ml. of water. AgCl 0.00017; AgBr 0.00004; AgI 0.00001.

Interferences.—Antimony, mercury, and lead interfere and should be removed if present.

Paper is separated in the first procedure as the carbon reduces the salt to metallic silver, causing low results.

Gooch.—If the asbestos fibre is poor, a loss of the fibre will occur during washing of the precipitate, causing low results.

Light.—Strong light will affect the salt causing the formation of the subhalide of silver and the liberation of chlorine. A drop of nitric followed by a drop of hydrochloric acid will restore the original form. This treatment is necessary only when a dark-colored salt is obtained by light action.

Large Samples.—It is frequently advisable to dissolve larger samples than stated. The solution is made to 500 ml. and a portion taken for analysis.

DETERMINATION AS SILVER CYANIDE

In the analysis of mercury, the nitric acid solution of the metal is nearly neutralized with a solution of sodium carbonate. Potassium cyanide solution is then added until the precipitate, which first forms, is dissolved. Then under a hood with strong draft, dilute nitric acid is added in slight excess of the quantity required to combine with the base in the amount of potassium cyanide present. The precipitate of silver cyanide, practically insoluble in dilute nitric or hydrocyanic acid, is coagulated by stirring or long standing and filtered from the cold solution of mercuric nitrate by use of a tared paper-bottomed Gooch crucible. The precipitate is washed with cold dilute nitric acid (1:10) until a test of the washings with hydrogen sulfide shows the absence of mercury. The crucible is dried at 100° C. to constant weight.

$$AgCN \times 0.8057 = Ag.$$

NOTES.—Determination of silver as metal through precipitation with hypophosphorous acid [8] as silver sulfide or as silver chromate [9] are methods of doubtful technical application.

[8] Mawrow and Mollow, Z. anorg. allgem. Chem., 61, 96 (1909).

[9] Gooch and Bosworth, Am. J. Sci., 27, 241 (1909).

ELECTROLYTIC METHOD[10]

According to the strength of the silver bath 10 or 20 ml. are filtered into a tared 200-ml. platinum dish and according to the greater or smaller excess of cyanide present, ½ to 1 gram of potassium cyanide in solution is added. The electrolyte diluted to about a half inch from the edge of the dish is kept, by a flame underneath, at a temperature of 60°–65° C. during the period of electrolysis at $N.D._{100} = 0.08$ amp.

Complete precipitation, which requires three to three and a half hours, is recognized by test with ammonium sulfide. Without interruption of the current, by use of a siphon, displacement of the electrolyte with water is accomplished. The dish is rinsed with alcohol and ether, dried at 100°, weighed and silver obtained calculated to grams per liter or cubic foot.

NOTES.—Benner and Ross[11] deposit 0.15 gram in twenty minutes with a current of 3 amperes from 50 ml. of electrolyte containing 8 grams potassium cyanide and 2 grams potassium hydrate on a 9-gram platinum gauze cathode.

Exner,[12] using a platinum dish as the cathode and a 2-in. diameter bowl-shaped spiral anode revolving 700 R.P.M., deposited 0.4900 gram from about 125 ml. of a hot electrolyte containing 2 grams potassium cyanide in ten minutes at $N.D._{100}$ 2 amps.

The above methods presume the absence of other metals precipitable under the conditions mentioned.

VOLUMETRIC METHODS FOR DETERMINATION OF SILVER

VOLHARD'S THIOCYANATE METHOD[13]

This method is especially adapted to the determination of silver in cold dilute nitric acid solution. The method is based on the greater affinity of silver ions than ferric for thiocyanate ions. When the silver has been precipitated as thiocyanate, the ferric indicator reacts with the thiocyanate producing the characteristic red color.

Reactions: $AgNO_3 + KCNS = KNO_3 + AgCNS$ ppt.
$Fe(NO_3)_3 + 3KCNS = 3KNO_3 + Fe(CNS)_3$ red.

NOTE.—Mercury and palladium, highly colored salts of cobalt and nickel, copper if over 60% in the sample, nitrous acid and chlorine interfere and should be absent.

[10] Langbein, "Electro-Deposition of Metals," 6th Ed.
[11] J. Am. Chem. Soc., 33, 1106 (1911).
[12] J. Am. Chem. Soc., 25, 900 (1903).
[13] Contributed by Wilfred W. Scott.

Ferric Indicator. ***Saturated Solution.***—Make 100 ml. of a saturated solution of ferric ammonium sulfate or ferric sulfate. Add sufficient HNO_3 (freed from nitrous acid by heating) to clear up the solution and produce a pale yellow color, .5 ml. of this reagent is used in a test. Ferric nitrate may be used in place of sulfate.

Standard Silver Solution.—A N/10 solution contains per liter 10.788 grams of silver, or 16.989 grams of $AgNO_3$. A solution containing 0.005 gram of Ag per ml. is a convenient strength.

Dissolve 1.0 gram of pure silver foil in 10 ml. of dilute HNO_3, 1 : 1.6 (sp.gr. 1.2). Boil to expel the nitrous oxides and dilute to 200 ml. One ml. will contain 0.005 gram of silver.

Thiocyanate Reagent.—Dissolve 7.4 grams NH_4CNS or 9.2 grams of KCNS in water and dilute to 1000 ml. Standardize the solution against the standard silver solution. Half this strength is used for the weaker silver solution above.

Standardization.—Measure 50 ml. of the standard silver solution into a beaker or an Erlenmeyer flask and dilute to 100 ml.

Add .5 ml. of the ferric indicator.

Titrate with the thiocyanate reagent until a permanent red tint is obtained. Each addition of the reagent will produce a temporary red color which fades immediately as long as any silver remains uncombined with the thiocyanate. A trace of excess of the reagent produces a permanent faint red color.

Note the ml. required and calculate the value of 1 ml. in terms of silver. Fifty ml. of the standard silver solution contains 0.25 g. of Ag.

Some prefer to have the thiocyanate exactly equal in strength to the silver solution. Should this be desired, dilute to the necessary volume and again standardize against the silver solution.

The value of 1 ml. should be recorded on the container.

DETERMINATION OF SILVER

Weigh 0.25–0.3 gram of the alloy and dissolve in an Erlenmeyer flask by addition of 5 ml. of dilute HNO_3 (sp.gr. 1.2). Heat to expel lower oxides.

Cool, dilute to about 100 ml. and add 5 ml. of the ferric indicator.

Titrate with the standard thiocyanate reagent to a permanent faint red color.

From the ml. of the reagent used, calculate the amount of silver present in the sample taken.

Divide the result by the amount of sample taken and multiply by 100 = % Ag in the alloy.

GAY-LUSSAC METHOD

This very accurate method is especially adapted to the valuation of silver bullion, but may be applied in principle to the determination of silver in a nitric acid solution which contains as little as 100 milligrams of the metal, providing the volume of the solution is not so large or color so deep as to make a precipitate of silver chloride equivalent to 0.1 milligram of silver indistinguishable. Metals that interfere are mercury and tin.

The method is founded upon the almost absolute insolubility of silver chloride or bromide in cold dilute nitric acid and the property of the precipitate becoming so completely coagulated through agitation that it settles speedily, leaving a liquid sufficiently clear to permit of observance of any precipitate produced by further addition of precipitant.

Reactions:

$$AgNO_3+NaCl=NaNO_3+AgCl\downarrow$$
$$AgNO_3+NaBr=NaNO_3+AgBr\downarrow$$

The use of a bromide is preferable to a chloride salt as a reagent, chiefly because on account of the greater insolubility of silver bromide, the end-point of the operation of titration is more sharply defined.

FIG. 100. Apparatus for Gay-Lussac Method.

The presence of free sulfuric acid is prejudicial to a very close determination, because of the volume of liquid required to keep silver sulfate in solution, and also because the result of agitation after addition of precipitant is apt to be a fine precipitate which does not readily settle.

The factor of volume change per degree change of temperature from 15 to 21° C. is approximately 0.00012; from 20 to 26°, 0.00019; from 25 to 31° C., 0.00024.

Although the approximate precipitating value should be known by previous test, it is the better practice to determine the exact value by running two or more checks of pure silver simultaneously with each batch of assays than to apply the temperature correction factor.

Apparatus.—The apparatus required consists of a pipette which will deliver approximately 100 ml. with an accuracy of not over 5 milligrams variation in weight of the standard solution at constant temperature between successive deliveries, 10 ml. burettes with glass stopcocks; and 8-oz. narrow mouth, round, flint-glass bottles with high, tightly fitting stoppers; the assay bottles

should be of a quality which will endure heating in a steam bath or on a hot plate.

Since the end-point by the Gay-Lussac method depends upon the observance of cessation of precipitation, it is evident, in order to avoid undue tediousness in its operation, that the silver content of the amount of sample taken for assay should be known within a few milligrams.

METHOD OF U. S. MINTS

U. S. MINT MODIFICATION OF THE GAY-LUSSAC METHOD FOR SILVER [14]

This method is used in all three of the United States Mints and the U. S. Assay Office, New York City, for determining silver in ingots and fine silver has been found very satisfactory both as regards speed and accuracy.

Standard Solutions.—Two standard salt solutions are regularly used in the determinations. The first is called a " normal " and the second a " decimal " solution.

The first or " normal " solution is made of such concentration that 100 ml. of it will precipitate exactly 1002 milligrams of silver. 5.43 grams of C.P. sodium chloride are dissolved in water and diluted to make one liter of solution. It is kept in a large 40-liter carboy and is siphoned off as needed.[15]

The decimal solution is made by diluting 100 ml. of the " normal " solution to a liter.

Standardization.—The normal solution must be standardized at frequent intervals because of temperature changes which affect the concentration of the solution. The factor of volume change per degree change of temperature from 15 to 21° C. is approximately 0.00012; from 20 to 26°, 0.00019; from 25 to 31°, 0.00024.

The standardization is carried out as follows:

Solution and Precipitation.—A " proof " of 1004 milligrams of fine silver is carefully weighed out, placed in a glass-stoppered 8-oz. bottle and dissolved in 10 ml. of 1 : 1 nitric acid on a hot plate. Then 100 ml. of " normal " salt solution, sufficient to precipitate 1002 grams of silver, are added from an upright stationary pipette. The pipette is filled by means of a siphon controlled by a stopcock convenient to the right hand. After filling, the left forefinger is placed over the pipette, the rubber hose connection removed from the bottom, and the bottle containing the dissolved proof placed underneath, when the forefinger is removed, allowing the contents to drain into the bottle, shaking the

[14] Communicated to W. W. Scott by F. C. Bond, Humid Assayer, Denver Mint, Colorado.

[15] Forty liters are made up at one time by the Denver Mint. The strength of the solution may be regulated by the size of the pipette used. At the Denver Mint 4.82608 grams per liter are taken of the C. P. NaCl, since the pipette delivers more than 100 ml.

bottle once or twice to mix the solution. Then 2 ml. of the decimal solution are added by means of a small pipette graduated in ml. and held in the hand, and the stoppered bottle is placed in the shaker.

The shaker violently agitates the solution and causes the precipitate to coagulate and settle. The bottle is removed after four minutes.

More agitation than is absolutely necessary should be avoided, due to the increasing tendency of the precipitate to become granular and settle slowly.

Titration.—The bottle containing the coagulated precipitate is best placed upon a shelf in a window through which only reflected light enters, at such a height that the top of the solution is upon a level with or slightly above the eye. The shelf is backed by a blackened board which covers the window under the shelf and extends nearly to the top of the bottle.

The bottle stands a moment to allow the precipitate to settle and 1 ml. of the decimal salt solution is added from the hand pipette. The solution is shaken by moving the top of the bottle through a small arc once or twice and the reading is taken after 10 seconds. A slight white cloud forming at the top of the solution and more pronounced when viewed from below constitutes a "show" and indicates that only a small portion of the ml. added was needed to precipitate the remaining silver. This is the desired condition for a proof.

The reading is taken as a "show," "quarter," "half," "three quarters," and "one"; according to the portion of the ml. of salt solution necessary to precipitate the remaining silver. If the cloud is deep enough to indicate that all of the ml. has been used, the bottle should be placed in the shaker and the precipitate coagulated, after which another ml. is added and the reading taken as before with the addition of one ml.

The assignment of the proper value to the precipitate is difficult for the novice and experience in comparison is of much more value than any description could be. However it may be stated that a slight precipitate extending through the upper half of the solution after a slight uniform shake should be called a "quarter," a precipitate of the same appearance throughout the solution is a "half," a heavier precipitate throughout is called "three quarters," while a still denser precipitate is read "one" and should be confirmed by shaking and adding another ml., which should yield a "show," a very faint cloudiness.

The "show" of the proof influences the reading of the determinations and its appearance should be kept constantly in mind, since a "quarter" on a determination means that one quarter of a ml. more of the decimal salt solution was used in precipitating silver than was used in the proof. Thus the proof reading or "show" is taken as zero and the concentration of the "normal" solution should be adjusted so that the proof gives as light a show as possible.

Procedure.—In the following determinations it is advisable to run a standard of proof silver side by side with the sample bullion for comparative purposes.

Fine Silver.—For silver bullion 998 parts fine or above a sample of 1005 milligrams is weighed out, dissolved, precipitated and titrated as described under Standardization.

In case 1 ml. was added, gave a heavy precipitate, was agitated and a second ml. added which gave a "half," the reading would be 1½ and the silver would be

$$\frac{1002+1\frac{1}{2}}{1005}=\frac{1003.5}{1005}=998.5 \text{ fine.}$$

In case a large number of samples are to be run, tables may be prepared for each fourth of a ml. which will make the above calculation unnecessary.

Coin Ingots.—In determining the silver in silver coins or in silver coin ingots as they come from the melting room, which are usually within 1½ points of 900 fine, the sample weighed is 1115 milligrams. The color given to the solution by the copper base need not interfere with the titration.

NOTES ON THE METHOD.—Determinations may be made on silver bullion of almost any grade if the approximate fineness is previously determined by fire assay or the Volhard method. It is ordinary practice to weigh up the sample at the next figure even five milligrams above that calculated. Thus if it is found from preliminary assay that 1082 milligrams of bullion will contain approximately 1002 milligrams of silver, 1085 milligrams will be weighed out for a sample.

Interfering Elements.—There are very few substances which will be found in bullion in sufficient quantity to interfere with the process. The presence of free sulfuric acid is detrimental to a very close determination.

The use of a bromide is considered as preferable to a chloride as a reagent but the chloride is commonly used.

An eyeshade assists in making the readings accurately.

The chloride precipitate is reduced to a blue subchloride on standing in the sunlight so that the bottle should be exposed to the light as little as possible.

A set of twelve samples, with the bottles transported in a suitable wire frame, is usually run at one time.

A decimal solution of silver nitrate of equal strength with the decimal salt solution may be used for back titration, however the end-point is less distinct and it is advisable to weigh out a larger sample.

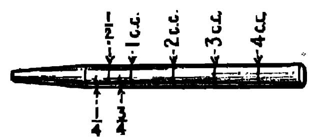


FIG. 101. Pipette.[16]

Duplicates are commonly run.

Tables giving the fineness for different classes of materials examined for each reading facilitate calculations and are recommended for use.

To determine the ¼, ½ and ¾, a beginner should have a pipette, graduated in 1 ml., holding 5 to 7 ml. length for hand use with one ml. divided in the ¼, ½, ⅓, and he should use the same until he is familiar with the density of precipitates produced by one ml. with silver equivalent to the above fractions.

WEIGHT TAKEN 1115 MG.

	0	1	2	3	4	5	6
0	896.9	897.7	898.6	899.6	900.4	901.3	900.2
½	897.1	898.0	898.9	809.8	900.7	901.6	902.5
½	897.3	898.2	899.1	900.0	900.9	901.8	902.7
¾	897.5	898.4	899.3	900.2	901.1	902.0	902.9

In the following table the left hand column represents the milligrams of bullion to be taken, the top line indicates the ml. of decimal solution required in addition to the 100 ml. of normal solution, the figures at the intersecting lines give the fineness of the bullion.

Ascertain the approximate fineness by a preliminary assay, consult the 0 column for the nearest corresponding figure slightly higher, the figure on the

[16] No pipette is of use in the practice of the Gay-Lussac method which shows any tendency to spatter at the beginning or ending, or yields a quickly following or clinging drop at the completion of discharge. The film of liquid adherent to the inner surface of the body of a good pipette will drain without sign of riculet effect and be retained by the capillary of the discharge tube for at least a minute.

left of this is the weight of bullion to be taken. Now if the test required, in addition to the 100-ml. normal solution, 4 ml. decimal solution and 1115 milligrams of bullion were taken, the fineness of the bullion would be 900.4. See table under Silver Coin Bullion.

HIGH GRADE BULLION

Milligrams of bullion	0	1	2	3	4	5	6	7	8	9	10
1000	1000.0										
1005	995.0	996.0	997.0	998.0	999.0	1000.0					
1010	990.1	991.1	992.1	993.1	994.1	995.0	996.0	997.0	998.0	999.0	1000.0
1015	985.2	986.2	987.2	988.2	989.2	990.1	991.1	992.1	993.1	994.1	995.1
1020	980.4	981.4	982.4	983.3	984.3	985.3	986.3	987.2	988.2	989.2	990.2
1025	975.6	976.6	977.6	978.6	979.5	980.5	981.5	982.4	983.4	984.4	985.4
1030	970.9	971.8	972.8	973.8	974.8	975.7	976.7	977.7	978.6	979.6	980.6
1035	966.2	967.1	968.1	969.1	970.0	971.0	972.0	972.9	973.9	974.9	975.8
1040	961.5	962.5	963.5	964.4	965.4	966.3	967.3	968.3	969.2	970.2	971.1
1045	956.9	957.9	958.8	959.8	960.8	961.7	962.7	963.6	964.6	965.5	966.5
1050	952.4	953.3	954.3	955.2	956.2	957.1	958.1	959.0	960.0	960.9	961.9
1055	947.9	948.8	949.8	950.7	951.7	952.6	953.5	954.5	955.4	956.4	957.3

SILVER COIN BULLION

	0	1	2	3	4	5	6	7	8	9	10
1095	913.2	914.2	915.1	916.0	917.0	917.8	918.7	919.8	920.5	921.5	922.4
1100	909.1	910.0	910.9	911.8	912.7	913.6	914.5	915.4	916.4	917.3	918.2
1105	905.0	905.9	906.8	907.7	908.6	909.5	910.4	911.3	912.2	913.1	914.0
1110	900.9	901.8	902.7	903.6	904.5	905.4	906.3	907.2	908.1	909.0	909.9
1115	896.9	897.8	898.6	899.5	900.4	901.3	902.2	903.1	904.0	904.9	905.8
1120	892.9	893.7	894.6	895.5	896.4	897.3	898.2	899.1	900.0	900.9	901.8
1125	888.9	889.8	890.7	891.6	892.4	893.3	894.2	895.1	896.0	896.9	897.8
1130	885.0	885.8	886.7	887.6	888.5	889.4	890.3	891.1	892.0	892.9	893.8
1135	881.1	881.9	882.8	883.7	884.6	885.5	886.3	887.2	888.1	889.0	889.9
1140	877.2	878.1	878.9	879.8	880.7	881.6	882.5	883.3	884.2	885.1	886.0
1145	873.4	874.2	875.1	876.0	876.9	877.7	878.6	879.5	880.3	881.2	882.1
1150	869.6	870.4	871.3	872.2	873.0	873.9	874.8	875.7	876.5	877.4	878.3

RECOVERY OF SILVER FROM SILVER RESIDUES

Convert the residues to silver chloride by treating with hydrochloric acid and filtering off the chloride and washing. Dissolve the chloride in ammonium hydroxide added in slight excess. Add sodium hyposulfite, $Na_2S_2O_4$ (not thiosulfate, $Na_2S_2O_3$). Metallic silver is formed. Thiosulfate gives silver sulfide. Photographers' residues containing " hypo " yield silver sulfide.

Titration of Silver with Bromide in Presence of an Adsorption Indicator. Fajans' Method.[17]—The nitric acid solution of the silver, in which the acidity does not exceed 0.5 N, is treated with a few drops of rhodamine 6 G ($C_{26}H_{27}O_3N_2Cl$) indicator and then titrated with a standard solution of

[17] K. Fajans and H. Wolff, Z. anorg. allegem. Chem., 137, 241 (1924).

potassium bromide. As long as the silver ion is in excess, the basic dyestuff is not appreciably absorbed by silver bromide. At the end-point the precipitate changes to a blue-violet color. The color change is distinct to a dilution as low as 0.01 N solution of silver.

COMBINATION METHODS

Combination of the operations of the Gay-Lussac and Volhard methods have been devised to avoid the tediousness incident to the performance of the Gay-Lussac method by the unexperienced. By the modified methods the amount of sample to be weighed out is determined by preliminary assay, and is dissolved in the same manner as in the practice of the Gay-Lussac method, but with the added precaution to decompose nitrous acid in the silver solution by gentle boiling when completion of the titration is to be accomplished by the Volhard method.

The operation of the combination methods consists briefly of precipitation of all but a few milligrams of silver by a standard solution of alkali thiocyanate, chloride or bromide added from the Stas pipette and estimation of the excess of silver with a decimal solution of thiocyanate or by a colorimetric or nephelometric method.

The procedure favored by the writer is to use a standard solution of potassium bromide as the pipette precipitant. After the liquid is cleared by shaking, it is decanted as completely as possible into a 500-ml. Erlenmeyer flask. The precipitate is washed by five 30-ml. portions of water containing a little nitrous-free nitric acid, each portion being shaken before decanting. Using the same amount of ferric indicator as in the check assays, decimal thiocyanate solution is added until not a very deep tint remains permanent after vigorous agitation. Decinormal silver solution is then added until the tint is discharged. When the assay is sufficiently free of copper or other colored salts to permit accurate matching of tints, the decanted liquid, which may contain particles of silver bromide without interference, is titrated with decimal thiocyanate to the appearance of a tint which will match that of the check assays. Except when colored salts are present in such quantity as to make recognition of the point of bleaching of the ferric thiocyanate coloration uncertain, the extreme range of error is 0.3 part per 1000.

For colorimetric method, see Smith, I. M. M. Bull. No. 28. Determination of the residual silver in the filtrate from the thoroughly washed silver bromide precipitate is practicable by use of a suitable nephelometric apparatus.[18]

DENIGE'S CYANIDE METHOD[19]

Silver which has been precipitated as chloride may be determined volumetrically by dissolving the precipitate with a measured quantity of a standard solution of potassium cyanide of about decinormal strength.

$$AgCl + 2KCN = KAg(CN)_2 + KCl.$$

Potassium iodide is then added and the excess of standard potassium cyanide solution determined by addition of potassium iodide and titration to the first appearance of a permanent precipitate with decimormal silver nitrate.

$$AgNO_3 + KI = AgI + KNO_3; \quad AgI + 2KCN = KAg(CN)_2 = KI.$$

[18] Richards and Wells, Am. Chem. J., 235, 1903; Richards, *ibid.*, 35, 510, 1906; Richards, Com. 8th Int. Cong. Ap. Chem., Sec. 1, 423.

[19] Clennell, "The Cyanide Handbook," 433. London, 1911.

NOTES.—If the last portion of the precipitate of silver chloride dissolves with difficulty in the potassium cyanide, the liquid may be decanted into another beaker and solution completed with ammonia. The solutions are combined.

MISCELLANEOUS VOLUMETRIC METHODS

Silver may be determined by addition from a burette of a portion of a known volume of its neutral or slightly acid solution to a standard solution of sodium chloride which contains a little potassium chromate or bichromate and sufficient chlorine-free magnesium oxide emulsion to neutralize free acid. The end-point is indicated by the formation of a reddish or brown precipitate.

By Pisani's Method [20] a standard solution of iodide of starch is added to a very dilute neutral solution of nitrate of silver until the fluid becomes permanently blue.

By Vogel's Modification of Pisani's Method,[21] the silver solution, which may contain free acid, is titrated with standard starch iodide solution after addition of nitric acid containing nitrous acid.

By Andrews' Modification,[22] the standard solution of starch is added to a solution of silver nitrate which contains so much ferrous nitrate or sulfate that iron will be in excess of the silver present.

$$2AgNO_3+2Fe(NO_3)_2+I_2=2AgI+2Fe(NO_3)_3$$

By Gooch and Bosworth's Method,[23] silver is determined by precipitating with an excess of potassium chromate, dissolving the precipitate in ammonia, reprecipitating by boiling to low volume and determining iodometrically either the chromate ion combined with the silver, or that remaining after precipitating the silver with a known amount of standard potassium chromate.[24]

NEPHELOMETRIC METHOD

This method is practicable for the determination of a small concentration of silver in a clear and colorless liquid. Less than 2 milligrams of silver can be estimated with considerable accuracy by matching the opalescence produced by a drop of hydrochloric acid with that from a known quantity in a liquid of the same volume, depth and temperature. Intensity of opalescence attains the maximum in about five minutes after precipitation. Standard silver solution is made by dissolving 500 milligrams standard silver (see Preparation at close of chapter) with several ml. of dilute nitric in a liter flask and making the solution up to the mark. For most technical determinations the apparatus may consist of clear glass cylinders (color tubes) of suitable size. More accuracy can be arrived at by use of a nephelometer of refined construction, for example [25] the combination of a projection lantern and a Duboscq colorimeter.

[20] Robière, Bull. soc. chim., **17**, 306 (1915); J. Soc. Chem. Ind., **34**, 1073 (1915).
[21] Fresenius, "Quantitative Analysis."
[22] Z. anorg. allgem. Chem., **26**, 175 (1901).
[23] Am. J. Sci., **27**, 302 (1909).
[24] C. A., **13**, 1735, 1909.
[25] Wells, Am. Chem. J., **35**, 99, 508 (1906); Richards, Am. Chem. J., **35**, 510 (1906); Dienert, Compt. rend., **158**, 1117 (1914).

Preparation of Pure Silver.—The volumetric methods used for the determination of high percentages of silver, employ solutions which should be standardized by metal of the highest purity. For the preparation of this metal, the electrolytic method as described below is preferred by laboratories which are suitably equipped.

For the manufacture of a large quantity—several pounds—a basket-like support for the anode is made of several glass rods bent so that they will hang from the rim of a tall 1000-ml. or larger beaker or battery jar and dip into the receptacle about an inch. Smaller anodes may be supported by the positive wire or by a cloth bag fixed in place by a string under the flare of the rim of the beaker. In any arrangement for the support of the anode, allowance of room should be made for the introduction and free movement of an L-shaped stirring rod.

The cathode may consist of sheet silver or of platinum foil, and lies flat on the bottom of the beaker. The immersed length of the silver or platinum wire leading from the cathode should be covered with rubber tubing.

Commercial silver, usually about 990 fine, may be used for the anode, but by retreatment of the deposit, very impure silver may be used, providing that the quantity of tellurium present is very low. The presence of tellurium will exhibit itself in the impossibility of obtaining the desired coarsely crystalline deposit.

Tellurium in moderate quantities may be removed by melting the silver in a crucible or scorifier, adding niter, permitting the silver to nearly freeze, raising the temperature and pouring into a hot crucible or scorifier in which the operation is repeated, preferably in a muffle furnace, until the surface of the silver is without streaks or spots when cooled to near freezing. An oxidizing atmosphere about the molten metal should be maintained. On the basis of 172 grams silver per cubic inch an anode mould for any convenient amount of silver may be shaped from 4-in. pieces of 1-in. square rod on a smooth iron plate. Just before the anode bar sets in the mould, a silver terminal strip or wire is plunged into it.

After coating the contact wire or strip and the surface of the anode about it with sealing wax, the anode is wrapped with filter paper, held firmly in place by string or rubber bands. If the anode weighs half a pound or more, the anode is also wrapped with cotton flannel which has been washed with water until free of chloride. A porous dish, cylinder or filter cone can be used instead of filter paper and cloth.

The electrolyte contains about 4% of C.P. silver nitrate and half a per cent of chlorine-free nitric acid in distilled water, and fills the beaker or jar so it wets only the lower surface of the anode.

The current, of about 0.1 ampere per square inch of cathode surface at the start, is raised after deposition has proceeded for a few minutes to the limit at which a coarsely crystalline deposit can be maintained.

Inasmuch as the electrolysis proceeds at a rate of 4 grams per ampere hour, some attention is required to break up short circuits and to pack down the rather bulky deposit. The deposit, if coarse, can be washed very easily free of electrolyte, and after heating to near redness is in the form preferred for use by many assayers.

Other methods which may be employed consist of dissolving the crude silver with nitric acid about 1.20 sp.gr. or with hot concentrated sulfuric acid, if platinum is present, separating the gold and platinum by filtration, precipitating AgCl with not too large an excess of HCl, stirring the precipitate until it coagulates, washing repeatedly with hot water until a washing is obtained which shows no precipitate with H_2S, reducing the silver chloride by contact with pure zinc, wrought iron or the silver terminal of a carbon-silver couple aluminum foil, and washing with hot dilute HCl until a test of the decanted liquid indicates absence of the precipitating element. The dried silver, mixed with about 1% of dry sodium carbonate, is packed into a clay crucible, the inside of which has been glazed with borax glass and covered with a layer of crushed charcoal.

The sodium carbonate is omitted in case it is desired to melt silver refined by electrolysis.

The silver melted in the tightly covered crucible is poured into an iron mould which has been chalked or black leaded.

By Knorr's method,[26] a solution of silver nitrate from which excess of nitric acid has been removed by evaporation is freed of metallic impurities by adding enough sodium carbonate to precipitate one-tenth of the silver, boiling and filtering. The silver in the

[26] Liddell, "Metallurgists and Chemists' Handbook." McGraw-Hill, 1918.

filtrate is precipitated by sodium carbonate and the precipitate decomposed without addition of reducing reagent, by melting in a crucible. Excess sodium carbonate carried down with the precipitate of silver carbonate will cover the fusion and such as adheres tightly to the metal is readily removed by hydrochloric acid. The metal should be smelted under charcoal.

If the cover of the charcoal is omitted or burned away during the fusion, the molten metal is capable of absorbing oxygen from the atmosphere to the extent of about 0.25% of its weight. This gas is expelled during the passage of the metal into the solid state and produces a casting which cannot be rolled into smooth sheets.

The most convenient size and shape of castings for rolling is but little larger than a lead pencil. Before rolling, the casting is cleaned of particles of the mould wash. After rolling to about cardboard thickness, the sheets may be cut up into strips of convenient size and length, then digested with dilute hydrochloric acid (1 to 5 of water) washed with ammonia and finally with pure water.

The silver then should be dried and annealed by heating to redness. It is best preserved in a glass-stoppered, salt-mouth bottle and should be exposed to laboratory atmosphere as little as possible.

The purity of each batch of silver made should be compared by use of the Gay-Lussac method with standard silver, the purity of which has been determined by analysis of a 50- or 100-g. portion for Se and Te, As, Sb, Pb, Cu, Au, and the element employed in reducing silver chloride, if the reduction method was followed in the manufacture of the metal.

A considerable portion of this chapter was contributed by W. G. Derby, who for many years was chief assayer and research chemist of the Nichol's Copper Company, New York.

THE FIRE ASSAY FOR GOLD AND SILVER[1]

Definitions.—*Fire assaying* is a branch of quantitative chemical analysis in which metals are determined in ores and metallurgical products by extracting and weighing them in the metallic state. The methods employed involve slag-melting temperatures and the use of reducing, oxidizing and fluxing reagents, and are in principle the same as those used in metallurgy.

The metals ordinarily determined by fire assaying are gold, silver and platinum. This method can not be recommended for the baser metals except as a means of concentration, for example of bismuth by means of lead, or of isolation of tin or white metals in preparing a sample of dross for wet analysis.

An *ore* is a mineral aggregate from which one or more metals can be extracted at a profit.

Metallurgical products include a large number of metal-bearing mixtures and compounds, ranging from high grade gold and silver bullion to very weak cyanide and sulfate solutions.

The constituents of an ore are usually divided into two general classes, the valuable minerals containing the *metals*, and the non-valuable minerals or *gangue*. A similar classification can be made in the case of many metallurgical products. In gold and silver bullion and other alloys most of the components are metallic, and the assaying problems involve mainly the separation of metals. Selenium (and at times Tellurium) is found in certain types of Doré Bullion.

GENERAL OUTLINE

With ores and metallurgical products containing non-metallic elements the process consists, briefly, in the production of two liquids, liquid lead containing the valuable metals, and liquid slag containing the waste matter or gangue. The two liquids separate from each other by reason of the great difference in specific gravity and insolubility in each other. The valuable metals are separated from the lead and from each other by taking advantage of differences in chemical properties. The slag may frequently be discarded,

[1] Original chapter by the late Irving A. Palmer, Professor of Metallurgy, Colorado School of Mines. Revised in accordance with suggestions made by T. A. Wright, Technical Director, Lucius Pitkin, Inc.

but it is often necessary to run corrections to recover the silver and gold invariably lost in slags and cupels; hence some slags must be saved for this purpose.

In the operation of the process the gold and silver, and platinum metals, if present, are collected from the metal-bearing portion of the ore or metallurgical product by means of molten lead reduced from litharge or lead oxide. The descending " rain " of tiny droplets of lead reduced from the litharge acts as a collector of the gold, silver and platinum metals. Therefore the litharge and all other additions should be substantially free of silver, bismuth, antimony and thallium, or else having a silver increment known to be negligible or exactly determinable on occasion, which is often necessary. The gangue is converted into a fusible slag by means of reagents known as fluxes.

The effectiveness of the fire assay in separating gold, silver and platinum from ores and metallurgical products depends upon two properties of these metals: first, their weak affinity for non-metallic elements, especially at high temperatures, and second, their very great affinity for molten lead. The collection of the precious metals in the lead, therefore, is the simplest part of the process. The fluxing of the gangue is much more difficult, and requires considerable knowledge and skill. If the fluxing is properly performed, the collection of the valuable metals usually takes care of itself. It is often necessary to add silver to assist the recovery of the gold by acting as a collector, and by reducing the loss of gold in the cupel, and to permit the subsequent parting operation to be effective.

Reagents.—A flux is a substance which when heated in contact with some difficulty fusible compound either combines with it or takes it into solution, in each case producing a compound or mixture which is easily fusible at ordinary furnace temperatures. The principal fluxes and other reagents used in fire assaying are described in the following paragraphs.

Litharge or oxide of lead, PbO, melting point 883° C., has several important uses. It furnishes the lead which collects the previous metals; it readily combines with silica, producing easily fusible silicates; and it acts as an oxidizing and desulfurizing agent. It is a very strong basic flux.

Sodium carbonate, Na_2CO_3, melting point 852° C., is a powerful basic flux. It combines with silica and alumina, producing fusible silicates and aluminates. When molten it has the property of dissolving or holding in suspension a number of refractory gangue materials. To some extent, also, it acts as an oxidizing and desulfurizing agent. The use of anhydrous sodium carbonate is in general preferable, but the bicarbonate, $NaHCO_3$, is employed where greater gassing action is desirable, since the latter gives off twice as much carbon dioxide as the former per unit of silica fluxed. Potassium carbonate, K_2CO_3, melting point 894° C., is rarely used in fire assaying because of its greater cost.

Borax glass, $Na_2B_4O_7$, melting point 742° C., is an acid flux used for combining with or dissolving the basic and some of the acid constituents of the gangue, producing easily fusible complex borates and mixtures of borates and other compounds. Even silica dissolves to some extent in molten borax glass. An excessive amount of borax glass should be avoided where silver values are important because of the tendency toward low results due to loss of silver in the slag under these conditions.

Silica, SiO_2, melting point 1755° C., is a strong acid flux. It combines with metallic oxides and produces silicates which in many cases are considerably more fusible than silica itself.

Granulated lead or test lead (m.p. 327° C.) is used in the scorification assay, which is conducted under oxidizing conditions, and in which, therefore, litharge could not be employed as a source of lead.

Lead foil or sheet lead is used in the assay of gold and silver bullion.

For many purposes sheet lead may contain more silver or bismuth than test lead, although this is of course to be avoided if possible; the amount of sheet lead rarely exceeds 20 g. in good umpire practice as in Doré assays, or 10 g. in the combination fire and wet blister assays.

Flour is known as a reducing agent. It contains carbon, which reduces lead from litharge. Charcoal was formerly used for this purpose, but is not so convenient.

Starch is a convenient reducing agent and its use is common practice.

Argol or crude cream of tartar, $KHC_4H_4O_6$, is both a basic flux and a reducing agent. On being heated it decomposes as follows:

$$2KHC_4H_4O_6 + \text{heat} \rightarrow K_2O + 5H_2O + 6CO + 2C.$$

It is effective in assays requiring strong reducing action and low temperatures.

Iron is sometimes used as a desulfurizing and reducing agent. It decomposes most of the heavy sulfides, yielding the metals and iron sulfide.

Potassium nitrate, KNO_3, melting point 339° C., is a powerful oxidizing agent. It is used to neutralize the effect of an excess of reducing substances in the material to be assayed. High sulfur ores, if assayed without previous roasting, require the addition of nitre to the charge. In contact with a reducing agent two molecules of potassium nitrate give up five atoms of oxygen, as shown in the following equation:

$$4KNO_3 + 5C \rightarrow 2K_2CO_3 + 3CO_2 + 2N_2.$$

The potassium oxide coming from the decomposition of the nitre acts as a basic flux.

Common salt, NaCl, melting point 819° C., is a neutral substance sometimes used as a cover for crucible fusions to exclude the air. When molten it rests on top of the charge and does not enter into it.

All of the reagents used must be pure and in a finely divided condition. Sodium carbonate shows a tendency to form lumps. These should be broken up and the entire mass put through a moderately fine screen.

Furnaces and Equipment.—The major operations of fire assaying are usually conducted in muffle furnaces. The muffle is a box-like receptacle; formerly fire clay was used but the silicon carbide muffle is rapidly displacing other types. The muffle is so placed in the furnace that all sides except the front are heated. There is a generous vent of rectangular shape in the back of the muffle. The refractory vessels containing the material to be assayed are placed in the muffle, and there is no direct contact with the fuel or its products of combustion. The fuel may be coal, oil, gasoline or gas.

Cupels.—The separation of the precious metals from the lead alloys produced in fire assaying is effected in small shallow vessels of bone ash, known

as *cupels*. The material consists mainly of calcium phosphate, small percentages of magnesium phosphate, calcium and magnesium fluoride and carbonate. It is a product of the burning of animal bones, preferably those of the sheep. It should be ground fine enough to pass a 40-mesh screen, in which

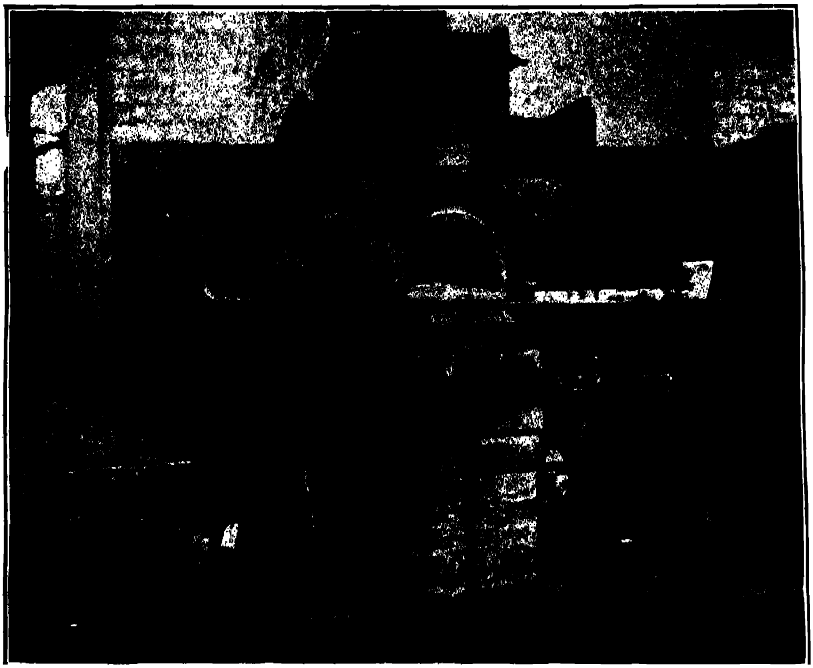


FIG. 102. Oil Muffle Furnace.

case about 50% of it will pass a 150-mesh screen. The cupels are made by moistening the bone ash with a small amount of water and then compressing it in the cupel mould, which consists essentially of a ring and die. The bone ash is forced into the shape desired at a considerable pressure, so as to insure sufficient rigidity in the cupel. The amount of water needed varies, but should be as low as possible. By using high pressures good cupels can be made from perfectly dry bone ash.

The requirements of a good cupel are that it should be infusible at ordinary furnace temperatures, that it should not be attacked by metallic oxides, that it should be porous, and that it should be sufficiently rigid to permit of considerable handling.

The question of cupel losses, other than those due to the purity and silver-gold ratio of the bead, is governed by a number of factors. Among these are cupel material, batch moisture, pressure, diameter and depth of cup, and contour of cup depression. All of these factors have been the basis of an extended study by J. T. King [2] which is commended to all assayers interested in silver losses. The study did not, however, include determination of lead retention,

[2] The Influence of Cupels on Silver Loss, J. T. King: Bulletin 147 (1934); 70 pp.; Univ. of Toronto.

an item not to be disregarded but which may in part offset silver absorption losses, nor did it include various gold-silver ratios. If, however, silver and gold are in the ratio of at least 5–1, gold absorption by good cupels, (copper not being present in unusual amount) is, for weights most often encountered, usually

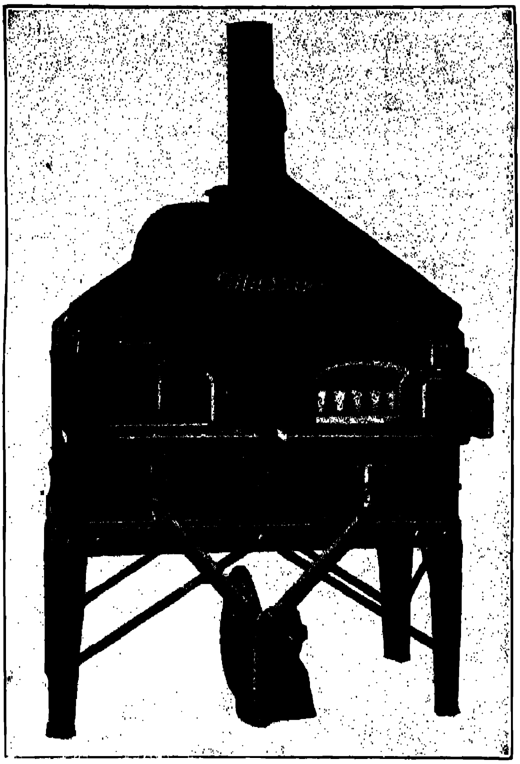


FIG. 103. Muffle Furnace.

negligible. Silver losses, in any event, for a cupellation to feathers will vary from about 1% for a bead 300 mg. or more up to about 4% for a bead of say 10 mg. weight. The loss is not a straight line relationship, however, for at 100 mg. the normal loss should be 1.90%±.15. For all the experimental losses determined by King (*ibid.*), however, less than .50% of the total loss could be attributed to volatilization. Reference should be made again to the original paper for the details and the twelve conclusions which are too extensive to quote.

Bone-ash cupels have been considered superior when made of a good grade bone-ash of properly proportioned particle size. In general, the grade known as XXX is preferable and King's recommendation of a water addition of 10 to 12% with a pressure of at least 800 lbs. per sq. in. at the die confirms good plant practice. Cupels should be dried slowly to avoid cracking but aging over a week is not necessary. A uniform height of about 1″ is indicated. Width varies with weight of lead button. Two sizes 1⅛″ and 1½″ are most common.

If cupels must be purchased or transported, or for some kinds of interplant control, a less fragile composite cupel of 70% bone-ash and 30% cement may be

used, but temperature control must be adjusted. Composite cupels are not favored for umpire assays or those of similar importance, though King (ibid) found that Silver losses at least were no higher than those made from bone-ash.

The Assay-Ton System.—As the precious metals are bought and sold by the Troy system of weights, and ores by the Avoirdupois system, considerable time would be lost in calculating assay results, were there no way of avoiding it. To simplify the calculation Prof. C. F. Chandler, of Columbia University, invented the assay-ton system of weights. The assay-ton is equal to $29,166\frac{2}{3}$ milligrams. As there are $29,166\frac{2}{3}$ Troy ounces in an Avoirdupois ton of 2000 pounds, the number of milligrams and fractions of a milligram of precious metals found in an assay-ton of ore corresponds to the number of Troy in an Avoirdupois ton.

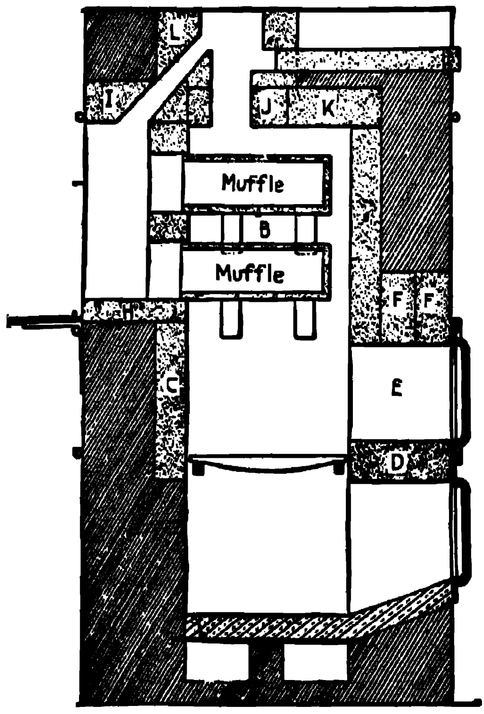


Fig. 104. Cross Section of Two-Muffle Assay Furnace.

Sampling.[3]—It goes without saying that good results in assaying presuppose accurate sampling. Silver is reported in assay certificates to the nearest tenth of an ounce; gold usually to the nearest one hundredth of an ounce. One tenth of an ounce means one part in 291,667; one hundredth of an ounce, one part in 2,916,667. In the preparation of the sample, therefore, the ratio between the weight of any fractional portion and the weight of the largest particle in it must be very large, so that the accidental inclusion of a number of rich pieces in any portion shall not affect the results beyond the limits of

[3] D. Brunton, Am. Inst. Mining Engrs., 40, 567–596 (1911); F. P. Dewey, Orig. Commun., 8th Internat. Cong. Appl. Chem., 1, 155.

error in assaying. Grinding to too fine a mesh should be avoided. From 80 to 120 mesh is probably the best range. The density of gold is so much greater than that of the country rock that segregation may occur on certain types of ore, if the grinding is too fine. The heat generated may volatilize sulfur as SO_2 or cause oxidation of other constituents to occur; this is of importance in rich material.

The division of the sample can often be done most precisely with Jones Samplers, the size of which is in relationship to the volume of the material to be divided.

Balances and Weights.—The balances used in fire assaying are somewhat different from those found in chemical laboratories. They are known as flux, pulp and assay balances. The assay balances are for weighing the gold and silver, often exceedingly small in amount, and are the most delicate type of commercial balances made. They should be quick in action and not liable to changes in adjustment. The beam should be short, light and rigid. The balance should be sensitive to 0.005 milligram at least. It need not have a capacity of more than 1.0 gram but should be accurate with that load.

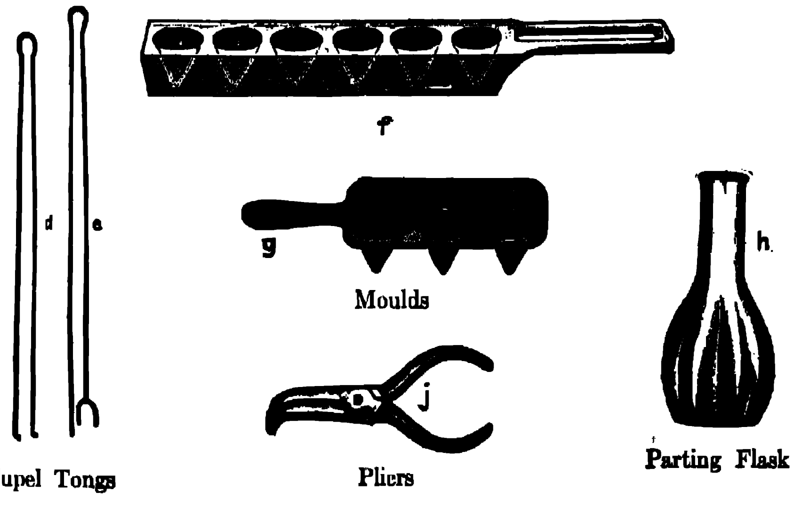


FIG. 105. Apparatus for Fire Assay.

In large laboratories separate balances are furnished for weighing the gold. These balances should be adjusted before each weighing and should be handled with the greatest of care. In the assay of gold ores, when using a half assay-ton portion, every error of .01 milligram in weighing the gold means a variation in the value of the ore of forty cents per ton.

It is desirable that a set of Bureau of Standards certified weights (1 g. to 1 mg.) be secured, and used for checking the weights used in routine work, at regular intervals; the standards should be sent back occasionally for restandardization. Weights should be handled only with bone tweezers, and with every precaution to avoid change in their mass.

The Crucible Assay.—This method of fire assaying is adapted to the great majority of gold and silver ores and to many metallurgical products. The

process consists in treating a weighed portion of the sample, carefully mixed with the necessary reagents, in a fire-clay crucible. In order to do this effectively the character of the material to be assayed must be known. Thus, ores may be oxides or sulfides. They may be basic, acid or neutral. They may be strongly oxidizing or strongly reducing. Each case requires a particular method of treatment.

The amount of sample of ores usually taken is one half assay-ton, run in duplicate. Twenty-gram fire-clay crucibles are used, that is, crucibles capable of holding twenty grams of ore and the necessary reagents. In most cases the total charge will fill the crucible to within one inch of the top. For jewelers' sweeps the sample is no larger than one-quarter assay ton, and for some types of slimes and precipitates which can be subjected to crucible assays, no more than one-tenth or even in certain instances one-twentieth of an assay ton should be used.

Lead Reduction with Oxidized Ores.—Experience has shown that the best results are obtained when the lead reduced from the charge amounts to from 25 to 35 grams. If the ore is oxidized, a reducing agent must be added to precipitate the necessary lead. Flour is the reagent ordinarily used although charcoal or argol can be substituted for it. The lead is reduced according to the following equation:

$$2PbO + C \rightarrow 2Pb + CO_2.$$

That is, 12 parts of carbon theoretically will reduce 414 parts of lead from litharge. Hence, the theoretical reducing power of carbon is 414/12 or 34.5. In practice, the reducing power of charcoal is found to range between 25 and 30, and that of flour from 10 to 12. Argol has a reducing power of about 8 or 9. In most oxidized ores, therefore, from 2½ to 3½ grams of flour will be required to reduce from 25 to 35 grams of lead from the litharge.

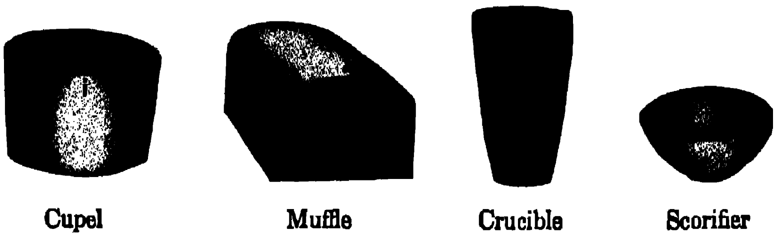


FIG. 106. Apparatus for Fire Assay.

If the ore contains ferric oxide, manganese dioxide, or some other easily reducible oxide, more flour must be added. Some iron-manganese ores require as much as 5 grams of flour to throw down the necessary lead. With unknown ores the right amount can be determined only by trial.

For jewelers' sweeps a minimum lead button of 80–90 g. is indicated, to be then scorified to 20–25 g. Sweeps are oxidizing in character since they consist of well burnt material and of iron and chromium oxides or other similar polishing agents.

Lead Reduction with Sulfide Ores.—In the case of ores containing sulfides, arsenides or other reducing substances, there will be a reduction of lead without

the addition of carbon. In fact it is usually necessary to add an oxidizing agent to prevent the precipitation of too much lead. The following reactions show the effect of a number of sulfide minerals when heated in contact with litharge and sodium carbonate.

(1) $PbS+3PbO+Na_2CO_3=4Pb+Na_2SO_4+CO_2$,
(2) $ZnS+4PbO+Na_2CO_3=4Pb+ZnO+Na_2SO_4+CO_2$,
(3) $2FeS_2+15PbO+4Na_2CO_3=15Pb+Fe_2O_3+4Na_2SO_4+4CO_2$.

The sodium carbonate induces the complete oxidation of the sulfur to SO_3, with the formation of the very stable compound sodium sulfate. In the absence of an alkaline carbonate most of the sulfur is oxidized to SO_2 only, and the amount of lead precipitated is correspondingly decreased.

Reaction (3) shows that pyrite has a greater reducing power than flour itself. If, therefore, a half-assay-ton of ore consisting mainly of pyrite were to be subjected to a crucible fusion, without the addition of some oxidizing agent, but with a large amount of litharge, anywhere from 100 to 150 grams of lead would be reduced. This would be entirely too much for the subsequent process of cupellation. In order to prevent the reduction of an excessive amount of lead, potassium nitrate is added to the charge. The following reactions show the oxidizing power of this reagent:

(4) $2KNO_3+5Pb=5PbO+K_2O+N_2$,
(5) $2FeS_2+6KNO_3=Fe_2O_3+4SO_3+3K_2O+3N_2$.

Reaction (4) shows that 202 parts of nitre will oxidize 1035 parts of lead to litharge. The theoretical oxidizing power of nitre, as measured against lead, is, therefore, 5.12. Reaction (5) when compared with reaction (3), given above, shows that 606 parts of nitre will oxidize the pyrite needed to reduce 3105 grams of lead from litharge. Here again the oxidizing power of nitre is shown to be 5.12. In practice, it is found to be somewhat less, more nearly 4.5.

The fire assay of sulfide ores, therefore, involves either a preliminary assay, or a calculation from the chemical analysis, in order to determine the amount of nitre to be added. With unknown ores it is better to make a preliminary fusion, using 5 grams of the ore, 75 grams of litharge, 20 grams of sodium carbonate and 10 grams of borax glass. The button of reduced lead is weighed and its weight divided by 5. This gives the reducing power of the ore. From this can be calculated the reducing power of one half assay-ton of the ore, and the amount of nitre necessary to add in order to cut down the weight of the reduced lead to about 30 grams. An excess of silica or borax glass decreases somewhat the amount of lead by causing the formation of difficulty reducible lead silicates or borates.

Amount of Litharge.—The amount of litharge for a half assay-ton charge usually ranges from 60 to 75 grams. Only about half of this is needed to produce the 25 to 35 grams of metallic lead used as the collector. The excess litharge serves to prevent the reduction of other base metals, such as antimony, bismuth, iron, copper and zinc, to help flux the silica, to act as a solvent for some of the refractory gangue materials, and to make sure that every particle of the ore in the crucible is in close proximity to one or more particles of litharge.

In special cases it may be advisable to use a very large excess of litharge, as in the assay of rich gold telluride ores, zinc precipitates and saturated cupels.

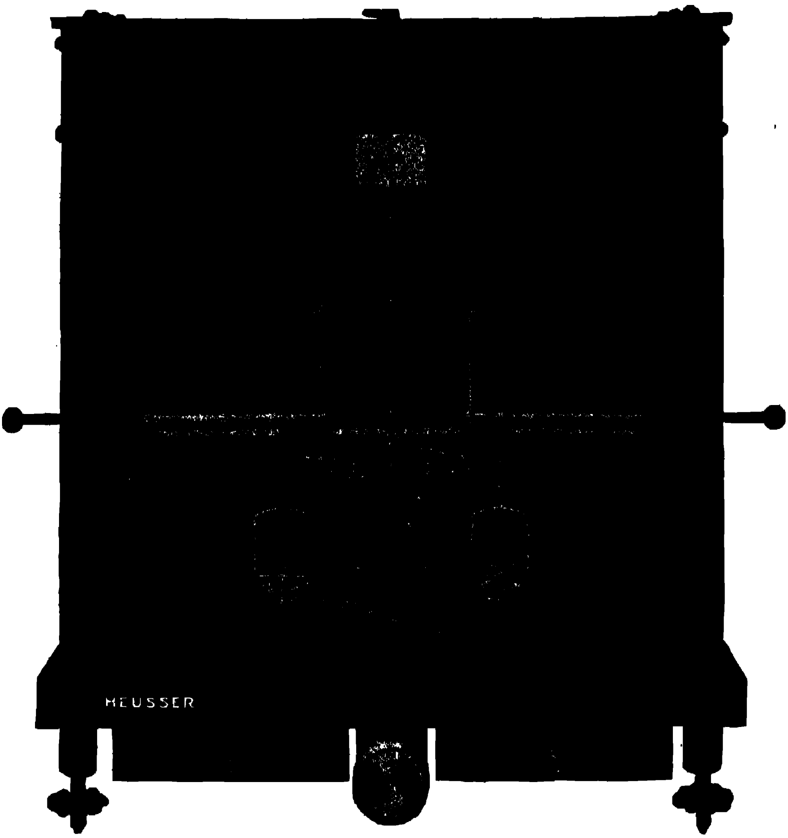


FIG. 107. Assay Balances for Small Weights.

Amount of Sodium Carbonate.—The amount of sodium carbonate to be used depends somewhat upon the character of the ore, although the modern practice is to use about the same quantity in assaying a great variety of ores and metallurgical products. The principal function of the sodium carbonate is to flux the silica and alumina, which are nearly always present in greater or less degree. The reactions are as follows:

$$(6)\ Na_2CO_3+SiO_2=Na_2SiO_3+CO_2,$$
$$(7)\ 2Na_2CO_3+SiO_2=Na_4SiO_4+2CO_2,$$
$$(8)\ Na_2CO_3+Al_2O_3=Na_2Al_2O_4+CO_2.$$

The two silicates and the aluminate are both quite fusible at ordinary furnace temperatures.

The silicates used in assaying and in metallurgy are usually classified according to the ratio between the oxygen in the acid radical and that in the base. Only four of these type silicates are of any practical importance. They are shown in the following table:

Sub-silicate	$4RO, SiO_2$
Mono- or singulo-silicate	$2RO, SiO_2$
Sesqui-silicate	$4RO, 3SiO_2$
Bi-silicate	RO, SiO_2

In the above silicates, the ratios are ½ to 1, 1 to 1, 1½ to 1, and 2 to 1, respectively.

Reactions (6) and (7) show that to flux one part of silica to bi-silicate and mono-silicate requires about 1¾ parts and 3½ parts, respectively, of sodium carbonate. If the half assay-ton of ore, therefore, consisted of almost pure quartz, it would take 25 grams of sodium carbonate to flux it to sodium bi-silicate, and 50 grams to flux it to the mono-silicate. As a matter of fact, the bi-silicate slag is satisfactory in this case. In general, the acid silicates have lower melting points but greater viscosity than the basic silicates. The excess litharge in the charge also combines with silica, and may thus produce more basic silicates. Moreover, a mixture of silicates usually has a lower melting point than that calculated from the melting points of its components.

Reaction (8) shows that 1 part of sodium carbonate is required to flux 1 part of alumina.

In practice from 30 to 35 grams of sodium carbonate are used in a half-assay-ton charge. In many cases this may seem to be a large excess. It must be remembered, however, that this reagent serves also to assist in the oxidation of the sulfides through the formation of sodium sulfate, that it has a solvent effect upon refractory oxides and other substances, and that it increases the bulk of the charge, thus protecting the ore from the action of the air and from the escape of the more volatile metals and their compounds. Being very fusible itself, an excess also serves to increase the fusibility of very refractory charges.

Amount of Borax Glass.—The rational formula of borax glass, $Na_2O, 2B_2O_3$, shows that it is an unsaturated compound and can take up more of the base. This base may be sodium oxide or one or more of the heavier oxides. The result of the addition is a fusible complex borate. This is shown in the following reaction:

(9) $Na_2O, 2B_2O_3 + 2CaO = Na_2O, 2CaO, 2B_2O_3$.

The compound produced is a sodium-calcium borate and shows the fluxing of .5 part of lime by one part of borax. The solvent power of borax glass for various substances has been referred to above. In practice it does not matter whether there is chemical combination or solution. What is desired is perfect liquidity at furnace temperatures.

The amount of borax glass ordinarily used in a half-assay-ton charge varies from 10 to 15 grams. If the ore is very basic and refractory, more borax should be used. It should be kept in mind that excess of borax tends to give low silver results.

Some assayers use silica in the assay of very basic ores. It is a good flux for iron and manganese oxides, producing fusible silicates. It is also very cheap. It cannot be used in excess, because of its very high melting point.

Assay of Slags.—The slags produced in crucible fusions in fire assaying are often very complex mixtures of silicates, borates, oxides and other compounds. In the molten state there can be chemical combination, solution and suspension, all at the same time. Ordinarily it is quite useless to attempt the formation

of a definite silicate or borate. If a sufficient amount of the proper fluxes is used, and a high temperature at the finish, there is usually no trouble in getting a good fusion. As a general rule the greater the complexity of the slag the lower its melting point.

For certain types of material of an intermediate metallurgical nature, such as slimes, precipitates, etc. commercial practice often calls for a corrected assay. This means that the slag from a set of fusions and scorifications must be saved and assayed separately with a new charge or as combined with the pulverized bone ash from the cupel. Beads from these slag and cupel correction assays at times run considerably lower in fineness than does a normal assay bead.

WEIGHING AND MIXING THE CHARGE

It is usually most convenient to mix the charge within the crucible. The fluxes should be put in first, the most bulky one at the bottom. They should be measured rather than weighed, in order to save time. Only the flour and nitre need to be measured accurately. The ore is carefully weighed on a pulp balance and placed on top of the fluxes. The mixing is best done by means of a steel spatula, and should be very thorough. Good mixing is shown by the uniform appearance of the charge. The fluxes should be free from lumps. The practice of using a salt or borax cover on the charge is not so common as it was. Ordinarily it is not necessary. When a salt cover is used in assaying rich ores, there is some danger of the production of volatile silver and gold chlorides. Borax glass as a cover is expensive.

Fusing the Charge.—The fusion of the charge is best conducted in a muffle furnace, although it can be made in a coke furnace, or even in a blacksmith's forge. The crucibles should be placed in the muffle when the latter is at a bright red heat. The temperature is then gradually raised until at the end of 45 minutes it reaches a light yellow heat, say 1050° C. Sulfide ores should be run rather more quickly than oxide ores, so as to oxidize the sulfides before they have a chance to melt down into a matte. If the heat be raised too rapidly, there is danger of boiling over, due to the large volume of gases liberated.

The crucible fusion may be divided roughly into three stages. There is first the preliminary heating stage, accompanied by some reduction of lead from litharge, the partial fusion and decomposition of nitre if present, the partial reduction of higher oxides, and some fluxing of silica by sodium carbonate and litharge. During the second stage most of the chemical reactions take place and the entire charge seems to be in a state of violent agitation. Lead is reduced from the litharge by flour, sulfur or other reducing agent, and the multitude of small shots pick up the adjacent particles of gold and silver. Gold tellurides and silver sulfides are decomposed by litharge, setting the metals free. Sodium carbonate and borax react upon the acid and basic constituents, respectively, of the charge, and produce slags. Alumina and other oxides either combine with these reagents or dissolve in the slag mixture. There is a copious evolution of gases, such as carbon dioxide, carbon monoxide, sulfur dioxide, and nitrogen. The third stage is known as the period of quiet fusion. It is for the purpose of completing the slag-forming reactions and of rendering the slag as liquid as possible. This enables all of the small particles

of lead to fall down through the slag, collecting the remaining traces of gold and silver. The latter are washed out of the slag much as a shower of rain sweeps the dust particles out of the air. The slag must be thoroughly liquid in order to insure a perfect separation from the lead.

A high temperature of the beginning of the fusion should be avoided, as it not only increases the chances of boiling over, but may cause some volatilization of compounds of the precious metals. After these metals are reduced and alloyed with lead, the temperature can be raised with less danger of loss. A row of empty crucibles or a prism of coke should be placed in front of the crucibles containing the fusions, and the muffle door should be kept closed.

The time required ranges from 40 to 55 minutes, according to conditions. A long-continued fusion at a low temperature usually means a small lead button and an imperfect collection of the gold and silver.

The period of quiet fusion should last about 10 to 15 minutes. The crucibles are then taken out of the muffle, tapped gently with a whirling motion, to collect stray shots of lead, and the contents poured into conical iron moulds. The greater part of the slag should be poured off first, so as to avoid splashing of the lead against the sides of the mould. When cold the lead buttons are taken out and hammered into rough cubes, so as to remove the adhering slag. If substantially free of copper the lead buttons are now ready for cupellation. It is not always advisable to pour the contents of a crucible charge. If Iridium, for example, is present or any of the other Platinum Group it is better practice as a rule to cool the charge in the crucible after tapping while still hot but slightly, however, to help assist settling. The crucible is then broken. Examine the slag for shot.

Crucible Charges.—It is impossible to give a crucible charge that would be satisfactory in every case. Modifications in the amount and kind of reagents must be made to suit the character of the material to be assayed. However, the variations are not so great as is generally supposed, and many assayers use stock fluxes for a great variety of ores and metallurgical products. Changes are made only when the conditions seem to require them.

The following tables gives the approximate amount of the different reagents used in an ordiary crucible fusion:

Ore	½ assay-ton
Sodium carbonate	25 to 35 grams
Borax glass	10 to 15 grams
Flour or Nitre	As required. (See Preliminary Assay)
Litharge	60 to 75 grams.

The Scorification Assay.—The scorification assay is used principally in those cases in which an undue amount of interfering base metals would be reduced along with the lead if crucible fusions were made. Thus, if a crucible fusion be made upon an ore containing copper or antimony, either of these two metals will be reduced along with the lead and produce a button which is difficult to cupel. Even with sulfide ores there is a considerable reduction of the copper or antimony, as is shown in the following reactions:

$$(10)\quad Cu_2S+3PbO+Na_2CO_3=Cu_2+3Pb+Na_2SO_4+CO_2,$$

$$(11)\quad Sb_2S_3+9PbO+3Na_2CO_3=Sb_2+9Pb+3Na_2SO_4+3CO_2.$$

Nickel and cobalt are reduced in the same way.

In many instances scorification is a natural sequence operation after the crucible fusion, in order to remove Cu, Sb, etc. Very high weights of lead—as much as 90–100 g.—are necessary per gram of high nickel optical or jewelry alloys. The combination of high lead and the maximum heat of the muffle is required to obtain a sufficiently fluid nickel-lead melt and slag, and thus minimize slag losses.

In the scorification assay the operations are carried out under oxidizing conditions so as to prevent the reduction of the interfering metals. Metallic lead is used as the collector and is added as such. The flux is mainly litharge, coming from the oxidation of the lead, with a small amount of borax.

The operation is conducted in shallow fire-clay dishes known as scorifiers, 3 inches in diameter. A 2½″ dish is used on the combination wet and fire assay. The amount of ore taken is usually 1/10 assay-ton, sometimes 1/5 or 1/20 assay-ton. About 25 grams of granulated lead are spread over the bottom of the scorifier and the ore then added and thoroughly mixed with the lead. The mixture is then covered with about 25 grams more of granulated lead and one gram of a 1 : 1 mixture of silica and borax glass. Usually from 5 to 20 portions of the ore are weighed up so as to lessen the chances of error. The scorifiers are placed in a muffle heated to redness and the door closed. As soon as the lead melts the door is opened, in order to admit air and increase the rapidity of the oxidation. The ore is seen to be floating on the lead. The latter begins to oxidize and the litharge produced in turn oxidizes the sulfides in the ore, assisted by the oxygen of the air. The temperature at this point must be low in order to prevent volatilization of gold and silver. The ore is not protected by a large bulk of fluxes as it is in the crucible assay. As the oxidation proceeds, a ring of slag, mainly litharge, begins to form around the bath of lead. The ore gradually disappears, the gold and silver going into the molten lead and the gangue combining with or dissolving in the litharge. Owing to the strong oxidizing conditions, most of the copper and practically all of the antimony present go into the slag. As the ring of slag increases, the temperature is raised. Finally, the lead becomes completely covered, and the muffle door is closed in order that the slag may become thoroughly liquid. The contents of the scorifiers are then poured into conical moulds, as in the case of the crucible fusions. The lead buttons should weigh from 15 to 20 grams. Very small buttons usually mean low results. With high copper material it is sometimes necessary to scorify two or three times and to use a large amount of lead. The buttons are cleaned and cupelled in the usual way.

The scorification assay is not adapted to ores containing volatile constituents, such as tellurides, arsenides and metallic zinc. Carbonates and highly oxidized ores are also unsuited to this method. If the ore contains much basic gangue it should not be scorified, as there is not enough acid flux to take care of it. Low grade gold ores are not usually assayed by scorification because of the small amount of ore taken. In practice the method is limited to the higher silver-bearing ores and metallurgical products containing considerable quantities of antimony, copper, nickel and cobalt. It is a standard method for the assay of copper matte. Scorification is also sometimes used to reduce the size of and to purify lead buttons produced in the crucible method.

Sometimes silver determinations in ores, especially those running 150 ounces or above, may best be handled by scorification rather than crucible fusion.

One half assay ton is divided between three scorifiers and combined on the second heat to one. The test lead used must be checked for freedom from Ag, Bi, Sb and Tl. Thallium in particular would go into the bead with the silver and give erroneous high results.

Some slimes and precipitates and silver sulfides are best assayed by initial scorification attack.

Cupellation.—Cupellation is the process by which the gold and silver are separated from the lead and other base metals with which they are alloyed. Design and make of cupel having been discussed under cupels, it remains to consider time, temperature and oxygen supply.

The lead buttons having been charged, the door should be closed to reduce the oxygen while melting and then immediately reopened. Even when opened it is not desirable to have such a strong draft that the "feathers" or litharge crystals formed are carried away. "Feathers" are the assayers' temperature control. Time varies from 20 to 25 minutes and losses for a finishing temperature of $875 \pm 5°$ C. will vary about $\pm.10$ for a 100 mg. silver bead.

In the cupellation process the lead is oxidized to litharge which is taken into the pores of the cupel by capillary attraction. This takes place because litharge is molten at the temperature of the operation. Most of the other base metal oxides are infusible at this temperature. When in moderate amounts, however, they dissolve in the liquid litharge and are carried into the cupel. If the lead contains much copper and antimony, the oxides of these latter metals accumulate on the cupel and may ruin the assay. Hence the need for scorification in these cases.

The cupels should be heated in the muffle for at least 20 minutes before putting in the lead buttons. Cupellations are best started at a bright red heat, say about 900° C. As soon as the buttons are put into the cupels, the muffle door should be closed. If the temperature is too low, an infusible oxide will form on the lead as soon as the latter is melted and refuse to go into the cupel. The disappearance of this film of oxide on further heating is referred to as the "*opening*" or "*uncovering*" of the lead. Sometimes it is necessary to hasten the opening by means of a burning stick of wood placed immediately over the cupel. This reduces the oxide and at the same time raises the temperature. When all of the cupellations are uncovered, the muffle door is opened and the temperature lowered rapidly to the lowest possible point at which the operation can proceed. This must be done because a temperature higher than necessary increases the loss of gold and silver. This loss occurs by absorption into the cupel and by volatilization. If the temperature falls too low, the buttons "freeze"; that is, the litharge, which melts at 883° C., solidifies on top of the liquid lead, which melts at 327° C., and the operation stops. The melting point varies with the ratio Pb:Au:Ag.

At first thought it would seem that a temperature slightly above 883° C. would be the proper one for cupellation. As a matter of fact the temperature of the muffle need not be above 750° C. This is due to the fact that the oxidation of the lead generates a considerable amount of heat, and the buttons are thus hotter than either the muffle or the cupels. A good indication of the right cupellation temperature is the formation of solid flakes of litharge, known as "feathers," upon the inner edge of the cupels. The volatilized litharge strikes

the comparatively cool bone ash and sublimes as flake crystals. If the beads contain platinum metals, it is not ordinarily desirable to cupel to "feathers," but rather to raise the temperature slightly above that normally necessary through the 21 to 23 minutes operation. Otherwise unusually large amounts of lead are retained. When change is made from the clay muffle to the silicon carbide muffle, the operator must learn to associate temperatures with a different series of colors.

The presence of impurities usually increases the loss of gold and silver, and adds to the difficulties of the operation. Copper or nickel in quantity may cause the buttons to freeze even at moderately high temperatures. Antimony causes the formation of a hard, infusible crust of lead antimonate which retains silver and which often splits the top of the cupel.

The surface of the lead in the cupel is convex, owing to the high surface tension of the metal. During cupellation the drops of molten litharge can be seen rolling off of the lead and disappearing into the cupel. The surface tension of the melted litharge is less than the attractive force of the bone ash. In scorification, where the vessel is not porous, the litharge forms a concave surface and climbs up the sides of the scorifier. This explains in part the high gold losses in the cupellation of lead containing gold and tellurium. Some of the gold telluride passes into the cupel just as in the case of litharge. Gold telluride is also more volatile than metallic gold.

As the operation proceeds, the lead and other base metals gradually oxidize and disappear. Copper and bismuth are less readily oxidized than lead, and hence tend to remain until most of the lead has gone. The presence of bismuth can be seen by the so-called bismuth ring, and even when this is not noticeable, the bead may still retain bismuth sufficient to reduce the fineness to a point requiring correction when large tonnages are involved. The temperature should be raised slightly at this point in order to prevent the buttons from solidifying before the base metals are completely oxidized. Small amounts of these metals usually remain, even in a well-conducted cupellation. The melting point of gold and silver being considerably higher than the temperature of the muffle, the buttons solidify soon after the base metals are gone. At the moment of solidification the buttons flash or "blick," owing to the release of the latent heat of fusion. If the buttons are large and consist mainly of silver, they may "*sprout*" or "*spit*" on being withdrawn quickly. This is due to dissolved oxygen which escapes when the button solidifies. The sprouting may be prevented by covering the silver button with a hot inverted cupel as soon as the cupellation is finished, and allowing the covered cupel to remain in the muffle for several minutes. This insures a slow cooling of the silver bead. After cooling the buttons are removed from the cupel by means of forceps and the adhering bone ash brushed off. The buttons are then weighed on an assay balance to the nearest one-tenth of a milligram. If a half-assay-ton of ore was used, the results multiplied by two equal the ounces per ton of combined gold and silver.

In cleaning buttons which are sometimes large enough to require squaring with a hammer on an anvil before cleansing with a stiff brush, rather than by compressing with pliers, the bottom of the button should be examined for roots, which are evidence of faulty cupel material or manufacture. Such buttons should be discarded.

Parting.—Parting is the separation of gold from silver in an alloy containing these metals, and is effected in fire assaying by means of nitric acid. This acid converts the silver into soluble silver nitrate, but is almost without action upon the gold. In order to part readily the alloy must contain at least twice as much silver as gold. Even at this ratio it is difficult to dissolve all of the silver. In practice, it is better to have a much larger proportion of silver, except in the assay of gold and silver bullion. If the buttons produced in the assay of an ore are known to contain enough gold to render parting difficult or impossible, they are subjected to the process known as *inquartation.* The buttons after weighing are wrapped with about 10 times their weight of pure silver foil in 3 to 5 grams of sheet lead and then cupelled. The resulting buttons are flattened and parted in the usual manner. It is preferable to add the necessary silver before cupelling at all as inquarted golds tend to be low.

An important point in parting is the strength of the acid. If a concentrated acid is used at first, the gold in the button is liable to break up into a fine powder which is difficult to manage without loss. By using a rather weak acid, containing 1 vol. concentrated HNO_3+5 vol. H_2O, the gold has a tendency to coalesce into a coherent mass which can be washed and weighed as one piece. "If the bead (e.g. from some slimes) contains Selenium, the use of a 1 : 9 first acid assists in minimizing 'flouring' of the gold." The treatment with weak acid is always followed by one with a stronger acid, in order to remove the last traces of silver. The second acid should be about 1.26 sp.gr., made by diluting the concentrated acid with its own volume of water. In the case of buttons containing a small proportion of gold, the first acid should be very weak, not more than 10% HNO_3. With more gold a stronger acid can be used, although the weak acid is usually effective, except when the buttons are very large.

The parting may be done in porcelain capsules preferably or in small glass flasks, known as parting flasks. Only a few ml. of acid are necessary. This should be heated to boiling and the flattened beads then dropped into it. Solution of the silver begins immediately. At the end of about 20 minutes, or when all visible action has ceased, the weak acid solution is decanted into a white casserole, carefully avoiding the loss of any gold. About 3 ml. of the stronger acid is now added to each flask or capsule and then heated almost to the boiling point. The heating is continued for at least 10 minutes, when most of the silver should be in solution. The acid is then poured off and the gold washed three times by decantation with chlorine-free water. If capsules are used, the water is drained out as completely as possible and the capsules then placed on a hot plate or in front of the muffle for drying. If parting flasks are used, a fire-clay annealing cup is inverted over the top of each completely filled flask and the flask then quickly reversed, allowing the gold to fall quietly into the annealing cup. After removing the flask by a quick side motion, the water is poured off of the gold and the cup placed on the hot plate. The final process is known as annealing. The capsules or annealing cups are placed in the muffle and heated to low redness for about 5 minutes. The heating causes the brownish-black spongy or fibrous gold to coalesce into a dense flake or bead having the characteristic yellow color of the metal. The annealing also serves to drive off any volatile impurities which may be present, and to render it easier to separate any specks of dust or dirt from the gold. After cooling the gold is weighed on a delicate balance to the nearest .01 milligram—with a little care

to the nearest .005 milligram. The weight of the gold is deducted from the weight of the button before parting and the difference represents the silver in the portion taken for assay.

In parting it is preferable to use for all ores and material low grade in character a weak acid, one of HNO_3 to six H_2O, for the first parting and a one to one acid for the second with no intermediate washing in between. It is advisable to add the hot "first" acid to the bead. This reduces flouring of the gold. It is also advisable to part in small casseroles as this gives a white background throughout the entire operation and the gold remains throughout until transferred to the pan. Washing should be by hot chlorine-free distilled water.

In doré, precipitates, slimes and rich gold-silver beads weighing up to as high as 990 milligrams to the gram sample the first parting should be in a stronger acid, one of acid to four of water. This should be followed by an intermediate washing with hot water by filling the casserole and decanting. The second acid treatment consists of a 20 minute simmer at incipient boiling with a still stronger acid, two of acid to one of H_2O. This is followed by at least two complete washings with hot water. This particular practice has been followed for many years with many thousands of proofs run as a control.

If the platinum metals are present, there should preferably be five or six times as much gold as platinum and twelve times as much silver as there is gold+platinum if the maximum amount of platinum is to be dissolved out in nitric acid on the first parting.

If the gold contains rhodium or iridium, it is advisable after weighing to dissolve in dilute one aqua regia to ten H_2O. The gold may either then be recovered by precipitation and weighed or it will often suffice, if the residue is not too floury, to decant, dry carefully and transfer it to a pan, weigh and deduct from the gold+platinum group metals to obtain a "true gold."

Parting along the lines indicated for the ordinary gold ore type of beads with the one to six followed by one to one acid should give a gold purity, if hot water is used, of 997.5 to 998.0, whereas cold water and weaker acid may give as low as 996.0. The finenesses given are on the assumption that no platinum group metals are present.

THE ASSAY OF BULLION

Bullion is an alloy of gold and silver with variable amounts of one or more of the base metals, and is the semi-final product of most non-ferrous metallurgical plants. In lead smelting this product is usually known as base bullion, in copper smelting as blister copper, and in amalgamation and cyanide processes as retort bullion or doré silver. The base metals may include antimony, arsenic, bismuth, cobalt, copper, lead, mercury, nickel and zinc. Small amounts of selenium and tellurium are usually present, as well as traces of the platinum group of metals. In all cases the assay of bullion resolves itself into a problem of the separation of metals from each other, there being practically no non-metallic elements present.

Bullion Sampling.—The sampling of bullion involves some difficulties not encountered in the sampling of ores. Most alloys on solidifying segregate to some extent, so that the cooled metal is never uniform in composition. Whenever possible the samples should be taken from the thoroughly stirred molten

alloy and then chilled quickly, either by pouring into water or by pouring into small moulds with thick metal sides and bottoms. When there is danger of oxidation, this method of course is not entirely satisfactory. In impure bullion there is often a very uneven distribution of the gold and silver, and it is necessary to drill or saw entirely through the bar in order to obtain accurate results. In copper anode plates and other forms of blister copper the plates or bars are drilled in series, so that the combined sample represents a proper percentage of drillings from all parts of each piece. Lead bullion is sometimes sampled in a similar manner, although in this case the bars are usually punched instead of being drilled. The modern tendency is to take melted samples of all metallic products, even in the case of blister copper.

The Assay of Lead Bullion.—The sampling of lead wherever possible should be by the "gum-drop method." These drops representing each stage of the casting process, and sampling process too, should be weighed as they come and not cut to a definite weight. The assay of lead bullion ordinarily involves only cupellation and parting. The bullion is often impure, however, and it may then be advisable to scorify the weighed portions before cupelling. If the sample contains much copper or antimony, it should always be scorified. The precious metal loss in scorification is less than it is in cupellation, especially in the case of an impure bullion requiring a high temperature in order to cupel it.

Lead bullion is usually run in four portions of one half assay-ton each or at times of approximately 1 A. T. each. The four silver buttons are weighed separately and if there is a satisfactory agreement in the weights, the average is taken and the result multiplied by two. The buttons are parted in pairs, thus saving time in washing and weighing. Great care should be exercised in the cupellation of lead bullion and in the subsequent parting, as the bullion is a high grade product, and ordinarily no correction is made for losses in the cupel or otherwise.

If for silver, high bismuth bullion is best dissolved immediately in dilute nitric acid with some hydrofluoric acid present and the silver precipitated as the bromide. Scorification then follows as usual in a combination method.

The Assay of Copper Bullion.—Copper bullion may be assayed by the scorification method, but the results are satisfactory only in the case of the gold. The silver obtained is always much too low. Most of the loss can be recovered by assaying the slag and cupels, but this requires additional time and materials.

The best way to determine gold and silver in copper bullion is to use the so-called combination method, in which the copper is first removed by solution in acid. Formerly nitric acid was used for this purpose, but it was found that the results were low in gold. There was a tendency for some of the gold to go into solution. The nitric acid method is a convenient way of determining the silver, as the copper dissolves very rapidly in nitric acid, and the precipitation of silver as chloride is very complete. With the increase of secondary metals certain types of silver-gold bearing blister or anodes may contain appreciable quantities of tin. If appreciable tin is present, it may be necessary to add hydrofluoric acid to a nitric acid determination of the silver and a bromide rather than a chloride precipitation may be advisable.

For the assay of both gold and silver the sulfuric acid-mercuric nitrate method is recommended. One assay-ton of the finely ground, well-mixed

copper borings is treated in a large beaker with 10 ml. of water and 10 ml. of a solution of mercuric nitrate containing 25 grams of mercury per liter. The beaker is well shaken so as to amalgamate the copper, and 80 or 100 ml. of concentrated sulfuric acid then added. The beaker is covered, placed on a hot plate and heated until all of the copper is dissolved. This will require from one to two hours, according to the temperature and fineness of the sample. The beaker is now removed and the solution is allowed to cool. One hundred ml. of cold water are added, the mixture stirred, and then 400 ml. of boiling water added, with further stirring until all copper sulfate has dissolved. A solution of common salt is now added, just sufficient to precipitate all of the silver and mercury. Only a slight excess must be used, as silver chloride is soluble in strong sodium chloride solution. The beaker is replaced on the hot plate and the contents boiled so as to coagulate the silver chloride. The beaker is then removed, the solution diluted to 600 ml. with cold water and allowed to settle. The solution is then filtered through double filter papers, and the beaker and filter washed with hot water. The beaker should be wiped out with a filter paper and this added to the material in the filter. The filter and its contents are now transferred to a 2½-inch glazed scorifier and the filter paper burned off at a low temperature, so as to avoid loss of silver. After the paper is burned off, 30 grams of test lead are added and the material scorified until 12 to 15 grams of lead remain. The scorifier is poured and the lead button cupelled at as low a temperature as possible. The gold and silver are parted in the usual way. The results are very precise.

The object of the mercuric nitrate is to hasten the solution of the copper by forming a galvanic couple. It prevents also the formation of copper sulfide which is insoluble in dilute sulfuric acid.

Assays should be made in duplicate or triplicate.

NOTES.—If the sulfuric acid-mercuric nitrate (sulfate) method is used, as is recommended and as is common practice, not only should the copper borings be finely ground but they should only be ground in a mill which will give sharp facets to the grindings. A dull mill rounds, compacts the copper, and results in an undue amount of undissolved bullion causing innumerable inter-laboratory and accounting differences. Some laboratories do not add any water to the copper borings in the 800 ml. beaker and they employ only 80 or 90 ml. of concentrated sulfuric rather than 100 ml. Care should be taken that sufficient heat be given on the particular hot plate used. If the burners are poor, it may be necessary to finish for a few moments over a free flame. The salt cake should be a dull grey and the supernatant sulfuric acid practically colorless unless the material is very foul, in which event it may be of the same general greenish tint found when the heating has not been complete. If the temperature is sufficiently high and the drillings are properly ground, 40 minutes to an hour heating may suffice for a one assay ton portion. If silver is low, it is often advisable to add 10 or 15 milligrams to each charge at the start.

Many laboratories do not use glazed scorifiers, but rather fit a small sheet of about 10 to 15 grams of lead foil which serves to protect the bottom of the crucible from wetting by the filter paper and subsequent spitting. Fourteen to 18 gram lead buttons are preferred by many to the 12 to 15 range. *Avoid* drafts during charring of the filter and contents.

THE ASSAY OF GOLD AND SILVER BULLION

In the fire assay of gold and silver bullion a correction must always be made for the metal losses, because of the great value of the bullion and because the refining losses on a commercial scale are considerably less than the losses in

assaying. The assays are, therefore, always run with a check or "proof center." The check is an artificial sample made up so as to have as nearly as possible the exact composition of the bullion to be assayed. Two checks and three portions of the bullion, all five of the same weight, are cupelled and parted under exactly the same conditions. The weights of gold and silver found in the bullion samples are then corrected by adding or subtracting the loss or gain experienced by the gold and silver in the checks. In the assay of gold bullion there is sometimes a gain in the weight of the gold, due to the imperfect elimination of the copper and silver. This, however, should be the same in both checks and bullion samples. Results are reported in "fineness" or parts per 1000.

Silver Bullion or Doré Bullion Assay.—Standard practice in umpiring doré bullion calls for running quadruplicates, the number of checks depending upon the number of lots of similar material being run. If only isolated samples are being assayed, then two proofs should be run. If a long series is being carried through, it will often suffice to have each position in each row of the furnace represented consecutively by a proof. Under this system a seven cupel row would call for proof units of seven. The standard umpire practice normally calls for one gram portions, which in the case of drilled (and more unhomogeneous) samples is little enough. Shot samples are ordinarily more uniform but even there one gram seems to be standard practice. The sample is wrapped in 10 grams of gold-silver-free sheet lead, placed in the hot cupel and melted. As soon as they have opened up 10 grams more, folded in a little "T" shaped strip, is carefully inserted to wash down the sides. Ordinarily 1½ to 1¾" cupels are used rather than the 1⅛" or 1¼" more common in ore work. In bullion carrying about 5 ppt. of gold, with silver from 800 to 900, the silver retention in the gold bead offsets the cupel gold absorption as has been verified by innumerable checks for many years.

Up to about 20 parts per thousand the proof will show a loss, thus necessitating a plus correction. In beads carrying 50 pts. of gold or over there is usually a surcharge, which of course results in a deduction or minus correction. Much depends on the gold : silver : copper ratio.

When proofs are made up it should be on the basis of a preliminary copper on a 200 milligram portion of the sample. Doré cupellations should not be conducted to as low a temperature as evidenced by feathers. This tends to give uneven retention of lead and erratic results. The higher temperature, which results in a greater silver loss due to greater volatilization of the silver, causes no harm as it is compensated for by the similar loss in the proof.

The beads are cleaned, weighed, flattened and parted. The first parting acid used should contain about 20% HNO_3, the second 50–66%. The amount of gold and silver loss in the checks is determined and the proper correction applied to the weights of gold and silver found in the bullion samples.

If the bullion contains antimony, the process must include scorification, which is applied to checks and samples as well. When bismuth, selenium or tellurium is present in quantity, the silver must be separated by means of solution in nitric acid and subsequent precipitation as chloride.

Gold Bullion Assay.—The assay of gold bullion is in principle the same as that of silver bullion. As the gold is usually in excess of the silver, however,

the process involves inquartation, with the use of a stronger first acid than when parting ordinary silver buttons.

U. S. Mint Method.—Sample portions of 500 milligrams are taken for assay. A preliminary cupellation is made as in the case of doré bullion. The amount of silver to be added for the final assay is determined by the touchstone method. The cupelled gold and silver button is rubbed on a piece of black jasper and the streak made compared with those made by alloys of known composition. This gives the fineness within 2%, which is close enough. A ratio of silver to gold of 2½ to 1 is used in making up the checks. If no copper is present, about 3 or 4% is added as it facilitates the removal of the last traces of lead in cupellation. The cupelled buttons are flattened by hammering, annealed at a red head, and then passed through a pair of jeweller's rolls, until they are converted into fillets about 2½ inches long and ½ inch wide. The fillets are again annealed and rolled up into "cornets" or spirals. Sufficient space should be left between the turns to permit of easy contact with the acid. The parting is done by boiling for 10 minutes in nitric acid of 1.28 sp.gr., and then transferring to another vessel containing acid of the same strength and boiling for 10 minutes longer. The cornets are then washed three times with distilled water, dried, annealed and weighed.

The proofs usually show a slight gain in the weight of the gold, so that the correction is made by subtracting the gain from the average weight of the gold found in the sample portions.

The gold after parting should be in one piece and have smooth edges, as otherwise there is danger of loss.

THE ASSAY OF CYANIDE SOLUTIONS

A number of methods have been devised for the determination of gold and silver in cyanide solutions. Only two of these methods will be described here.

Evaporation in Lead Tray.—This method is adapted to cyanide solutions containing only small amounts of base metals or other impurities. A small tray or boat is made of lead foil, capable of holding the amount of solution to be assayed. A wooden block or form is used to make the trays if many assays are required. The solution has about the same specific gravity as water, so that 29.2 ml. are assumed to be equal to an assay-ton. An amount of solution varying with its richness is put into the lead tray and slowly evaporated to dryness on the hot plate. The lead tray is then folded up and cupelled in the usual manner.

The Chiddey Method.—This method, first described by Alfred Chiddey, is adapted to almost every grade and character of cyanide solutions.

From 1 to 20 assay-tons of solution are heated in a beaker or evaporating dish. To the solution is added from 10 to 20 ml. of a 10% solution of lead acetate containing 40 ml. of acetic acid per liter. From ½ to 2 grams of zinc dust or zinc shavings is then added. The gold, silver and lead immediately begin to precipitate on the zinc. The solution is heated for about 20 to 25 minutes, but not to boiling. The lead should coalesce into a spongy mass. Boiling the solution is liable to break up the sponge. The excess zinc is now dissolved by adding slowly 20 ml. of hydrochloric acid of 1.12 sp.gr. The heating is continued until effervescence ceases. It may be necessary to stir

slightly in order to make sure that all zinc is dissolved. The solution is now decanted off and the lead sponge washed two or three times with water. The excess water is squeezed out of the sponge with the fingers, the sponge further dried by pressing between filter paper and then rolled into a ball with lead foil and the necessary silver for parting. A hole should be left in the lead foil for the escape of steam. The ball is then dried and cupelled.

As the lead sponge begins to break up and go into solution as soon as all of the zinc is dissolved, no time should be lost in decanting the solution after the zinc has disappeared.

Special Methods of Assay.—There are many ores and metallurgical products that require special methods for the determination of the gold and silver that they contain. It is impossible to refer to these methods here. A knowledge of the composition of the sample, however, will usually enable the skilled assayer to so modify the ordinary processes as to obtain satisfactory results.

For further details in regard to standard and special methods of fire assaying the reader is referred to such works as "A Manual of Fire Assaying," by Chas. H. Fulton, published in 1929, and "A Textbook of Fire Assaying," by Edward E. Bugbee, published in 1922.

DETERMINATION OF PLATINUM, PALLADIUM, GOLD AND SILVER [4]

Platinum, Palladium and Gold.[5]—Scorify the lead buttons from two or more ½ assay ton crucible fusions together, adding at least six times as much silver as the combined weight of the Pt, Pd and Au present, and cupel *hot*. In rich materials such as slimes or concentrates, two ½ assay ton fusions suffice, but low-grade ores may require 10 or more ½ assay ton fusions combined for each determination.

Part the silver beads with HNO_3 (1 : 6), followed by stronger parting acid (1 : 1) and wash with water as usual. All Pd goes into solution, together with considerable Pt. The residue consists of Au plus some Pt. Dissolve residue in strong *aqua regia* and reserve the solution (solution *A*). Precipitate the silver in the nitric-acid solution—containing Ag, Pd and some Pt—with HCl. Practically all the Pt will remain in solution; but the precipitated AgCl is pink in color and contains considerable Pd. Filter off the AgCl, scorify and cupel it and part again with HNO_3 (1 : 6); all should dissolve. Re-precipitate the Ag with HCl. The liquid now contains most of the remaining Pd, but some is co-precipitated with AgCl. Filter off the AgCl and add the filtrate to the first filtrate from AgCl. Again scorify and cupel the silver chloride,

[4] By A. M. Smoot, Eng. Mining J., 99, 701 (1915).
[5] See also the chapter on the Platinum Metals.

dissolving the silver in nitric acid as before and re-precipitating the silver as chloride. In most cases the filtrate from this silver chloride contains all the remaining Pd. If, however, the AgCl is distinctly pink, another separation must be made.

Unite all filtrates from AgCl precipitations and evaporate to small bulk, adding the *aqua-regia* solution of the Au and Pt (solution *A*). The liquid now contains all the Au, Pt and Pd present in the original ore, together with traces of Ag due to solubility of AgCl in excess of HCl, and also traces of Pb gathered from the lead retained in the silver buttons from several re-cupellations.

Evaporate the liquid to dryness on the steam bath; take up with dilute HCl (1 : 3) and evaporate again to dryness; take up with five drops of HCl and 40 ml. H_2O. Pay no attention to any insoluble residue of AgCl or $PbCl_2$.[6] Precipitate the gold by adding, say, 3 g. of oxalic acid to the solution and boiling it. Let stand over night and filter off the Au. If Pt and Pd are high, it is necessary to re-dissolve the Au in *aqua regia*, evaporating with HCl to dryness and repeating the oxalic-acid precipitation, uniting the filtrate with that from the first gold precipitation. Burn the filter containing the gold and scorify it with six times its weight of silver and a little test lead; cupel, part and weigh the gold as usual.

To the oxalic-acid filtrates from Au add 5 ml. of HCl and make volume up to 150 ml.; heat to boiling and precipitate Pt and Pd with a rapid current of H_2S in *hot* solution, passing the current of gas for some time and keeping the solution hot during precipitation. Filter and wash the Pt and Pd sulfides with H_2S water containing a little HCl. Wash the precipitate from the filter with a fine water jet into the original beaker; spread the filter paper (which will contain a small amount of precipitate impossible to wash off) with the precipitate side down over the lower side of a watch glass-cover. Add *aqua regia* to the precipitate in the beaker and place the cover on the beaker; warm gently to dissolve the Pt and Pd sulfides. The fumes arising from the acid dissolve the traces of Pt and Pd adhering to the filter paper. When solution is complete and filter paper is white, remove the watch-glass cover and wash the paper with hot dilute HCl thrown against it in a fine stream.

Evaporate the *aqua regia* solution to dryness, take up the residue with HCl and evaporate again to dryness to remove all HNO_3. Take up the residue with two or three drops of HCl and about 2 ml. of H_2O. The solution is usually perfectly clear, but it may be slightly cloudy owing to the presence of a little AgCl in it. No attention need be paid to this, however. Add 5 to 10 ml. of a saturated solution of NH_4Cl, stir well and allow to stand over night. Platinum is precipitated as ammonium-platinum chloride—$(NH_4)_2PtCl_6$. Filter and wash the precipitate with 20% NH_4Cl solution. All Pd passes into the filtrate which is reserved (solution *B*). Dissolve the Pt precipitate in boiling hot 5% H_2SO_4; heat the liquid to actual boiling and precipitate with H_2S as

[6] In materials rich in palladium the small amount of AgCl+$PbCl_2$ may be distinctly pink in color and retain weighable quantities of Pd. If this is the case, the Pd may be recovered in the solution from the nitric acid parting of the gold. To do this, precipitate the silver in this liquid by adding HCl, filter off the silver chloride and evaporate the filtrate to dryness. Take up with a drop of HCl and a little water, let stand over night and filter through a very small filter. This liquid may be added to solution *B* before precipitating palladium with glyoxime.

before, filtering and washing with H_2S water. Burn the filter and precipitate at a low temperature in a scorifier; add six times as much Ag as Pt, scorifying with lead, cupel and part the silver bead containing the platinum with H_2SO_4; decant off the silver solution and wash once with concentrated H_2SO_4, followed by 50% H_2SO_4 until practically all the silver is washed away; finally wash with water, anneal and weigh. A minute quantity of Ag is retained with the platinum, but it can usually be neglected. In very important work where the amount of platinum is large dissolve in *aqua regia*, evaporate the solution to dryness, take up with a drop of HCl, dilute largely with water and let the AgCl settle over night; filter on a small paper, cupel it with a little sheet lead and deduct the weight from the weight of platinum. This refinement need not be considered in materials running less than 15 or 20 oz. to the ton.

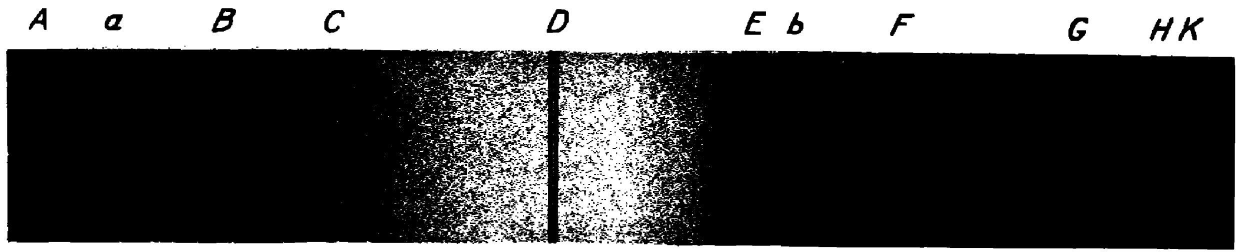
It may seem an unnecessary step to precipitate the platinum as sulfide, scorify it with silver and part it as described in the foregoing. General practice has been to ignite the ammonium-platinum-chloride precipitate and weigh the metallic residue. When this is done, however, there is danger of losing considerable platinum, which is carried away mechanically during the decomposition of the compound; furthermore, it is extremely difficult (if not impossible) to collect the finely divided residue for weighing, and the precipitate invariably contains lead and silver. Precipitation as sulfide, scorification and cupellation with excess silver and parting with sulfuric acid overcome the difficulties inherent in handling the ammonium precipitate.

The palladium is all contained in the filtrate and washings from the platinum ammonium-chloride precipitates (solution *B*). Add to this solution at least seven times as much dimethylglyoxime as there is Pd present (in any case, at least 0.1 gm. glyoxime). The precipitant should be dissolved in a mixture of two-thirds concentrated HCl and one-third water. Dilute the liquid to 250-300 ml., heat on a steam bath for half an hour and let stand over night. Pd is precipitated as a voluminous yellow, easily filtered glyoxime compound $C_8H_{14}N_4O_4Pd$, containing, when dried at 110° C., 31.689% of Pd. Filter the Pd precipitate on a weighed Gooch crucible and wash it, first, with dilute HCl, half and half, then with warm water and finally with alcohol; dry it at 110° to 115° C. and weigh. The disadvantage of weighing palladium on a Gooch crucible is overcome—at least to some extent—by the fact that the Pd compound contains a relatively small amount of Pd—less than one-third of its weight. This compound may also be weighed on carefully counterpoised papers; but it is better to use Gooch crucibles, if they are available, because of the relatively strong acid which is required for washing. The object in using half-and-half hydrochloric acid as a wash liquid is to dissolve out any excess of the glyoxime precipitant. This is easily soluble in moderately concentrated HCl, but is substantially insoluble in water.

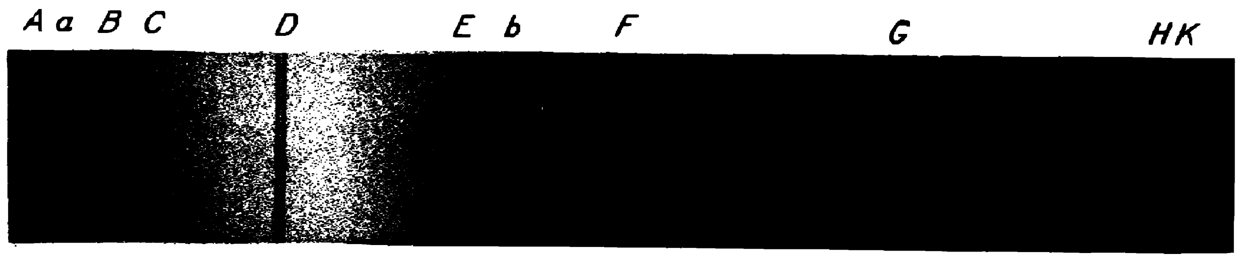
DETERMINATION OF SILVER IN ORES AND CONCENTRATES CONTAINING PLATINUM AND PALLADIUM

Make the usual crucible fusion on one-quarter, one-half or full assay ton, according to the amount of silver present. Instead of cupelling the lead button, hammer it free from slag and dissolve it in dilute nitric acid. Most of the silver passes into solution together with palladium, and perhaps a trace of platinum; but gold and most of the platinum remain insoluble. The gold and platinum retain an appreciable proportion of silver which cannot be washed out. Filter out the insoluble residue and wash it thoroughly with hot dilute nitric acid, followed by hot water. Scorify the residue once more with a little lead and dissolve the lead button as before, filtering into the beaker containing the first filtrate. In this liquid precipitate the silver as AgCl by adding standard NaCl in sufficient quantity; stir well, and if the amount of silver is small, add about ½ ml. of concentrated H_2SO_4 to form a precipitate of lead sulfate. Let the silver chloride, or the silver chloride plus lead sulfate, settle over night or until the supernatant liquid is clear; filter through double filter papers; ignite and scorify the residue of silver chloride with test lead.

If the amount of the palladium contained in the sample is small, the silver bead obtained by cupelling the lead button obtained by scorifying the silver chloride may be considered as sufficiently pure for ordinary purposes. It contains, of course, some palladium, and in accurate silver determinations the lead button from the first silver chloride precipitation should be re-dissolved and the silver re-precipitated, filtered and scorified as before. The amount of palladium retained after the second precipitation and scorification is so small as to be negligible.



Diffraction Grating Spectrum



Prismatic Spectrum

SODIUM AND THE OTHER ALKALI METALS[1]

LITHIUM, SODIUM, POTASSIUM, RUBIDIUM, CAESIUM

INTRODUCTION

The alkali metals—lithium, sodium, potassium, rubidium, and caesium—belong in the first group of the Periodic System and have similar properties. They all form strong bases, and their salts are generally soluble in water. Sodium and potassium are abundant elements, lithium is comparatively rare, and rubidium and caesium are classed as rare elements.

POTASSIUM

Potassium, K, *at.wt.* 39.096; *sp.gr.* 0.86; *m.p.* 62.3°; *b.p.* 760° C.; *oxides* K_2O, K_2O_2, K_2O_4

OCCURRENCE

Potassium is an abundant element widely disseminated in nature, forming 2.58% of known terrestrial matter.[2] It is found in many rocks and minerals, in practically all natural waters, in saline residues, and in ashes of plants. It is an important constituent of feldspar, mica, leucite, glauconite, alunite, sylvite, carnallite, kainite, poly-halite, and a good many other minerals.

Commercial sources of potassium include saline beds near Stassfort, Germany; in Alsace, France; near Carlsbad, New Mexico; and at Searles Lake, California.

DETECTION OF POTASSIUM

For the detection of potassium in insoluble compounds, bring the sample into solution by *one of the methods given under Solution of Sample. In other cases, prepare a concentrated solution of the material to be tested. Where only very small amounts of potassium are present, remove all the constituents from the*

[1] Chapter contributed by W. B. Hicks.
[2] Clarke, F. W., U. S. Geol. Survey Bull., 770, p. 36 (1924).

solution except the chlorides of magnesium and the alkalies as directed under Separations. In the presence of considerable amounts of potassium, small quantities of other constituents will not materially interfere with the flame and spectroscopic tests. After acidifying with hydrochloric acid, bring a drop of the solution to be tested into the non-luminous flame by means of a platinum wire and observe the color produced through a cobalt blue glass or a chrome alum light filter.[3] In the presence of potassium, a distinct reddish-violet coloration will be apparent. This must not be confused with the color caused by large amounts of sodium, which appear bluish-violet through the glass. Comparison with the coloration produced by pure salts is advisable. If necessary, confirm the results by examining the flame in the spectroscope. In the presence of a moderate amount of a volatile potassium compound, a bright red line will be readily seen in the red portion of the spectrum, and a less distinct violet line will be visible far out in the violet rays. Plate II, page 119.

Potassium may be identified by precipitation as cobaltic nitrite ($K_2NaCo(NO_2)_6$). For this purpose place a small quantity of the solution to be examined in a test tube, acidify slightly with acetic acid, add about an equal quantity of the sodium nitrite solution, prepared by dissolving 125 grams of sodium nitrite ($NaNO_2$) in 250 milliliters of distilled water, and about half as much of cobalt nitrate solution, prepared by dissolving 25 grams of cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) in 100 milliliters of distilled water and adding 50 milliliters of glacial acetic acid. Mix and allow the mixture to stand until effervescence ceases and the cherry-red solution is transparent. If an appreciable amount of potassium is present a yellow precipitate will have settled to the bottom of the test tube. By comparing the volume of the precipitate with that produced when a known quantity of potassium chloride is used, an idea of the amount of potassium present can be obtained. Ammonium salts produce a similar precipitate and must be previously removed.

Potassium chloroplatinate, perchlorate, acid tartrate, picrate, silicofluoride, phospho-tungstate, chloronitrotoluenesulfonate[4] and napthol yellow S,[5] are all sparingly soluble in water while the corresponding sodium salts are readily soluble. Precipitation of these compounds from solution may be used in the identification of potassium.

Silicate rocks and minerals may be tested for potassium by mixing the finely powdered material with an equal amount of pure calcium carbonate, moistening with hydrochloric acid, and examining a small amount of the wet mixture on a platinum loop in the flame with a light filter or the spectroscope.

[3] McCay, J. Am. Chem. Soc., 45, 2958 (1923).
[4] 6-Chloro-5-nitro-m-toluene sulfonate. Davies and Davies, J. Chem. Soc., 123, 2976 (1923).
[5] The potassium salt of 2,4-dinitro-1-napthol-7-sulfonic acid. Clark and Willits, Ind. Eng. Chem., Anal. Ed., 8, 209 (1936).

ESTIMATION OF POTASSIUM

The estimation of potassium is required in the analysis of rocks, minerals, soils, ashes of plants, waters, brines, saline residues, fertilizers, and many technical products. It is of particular importance in the analysis of fertilizers and soils.

SOLUTION OF SAMPLE

Procedure for Rocks and Other Insoluble Mineral Products.—For silicate rocks and minerals, glass, refractories, and other siliceous materials bring the potassium into solution along with the other alkali metals according to the J. Lawrence Smith method or the hydrofluoric acid method as directed on pages 882 and 883. For products which are dissolved by hydrochloric acid, effect the solution by digestion with the acid, expel the excess of acid by evaporation, and finally determine potassium by one of the methods given below. For alunite grind the powdered mineral and an equal quantity of pure silica and proceed as directed above for silicate rocks and minerals, finally determining the potassium by the Lindo-Gladding or Modified Chloroplatinate method.

Procedure for Soils.[6]—Follow the procedure given above for silicate rocks and minerals.

Procedure for Fertilizers.[6]—Mixed Fertilizers.—Place 2.5 grams of the sample upon a 12.5 cm. filter paper and wash with successive small portions of boiling water into a 250 ml. volumetric flask until the filtrate amounts to about 200 ml. Add to the hot solution a slight excess of strong ammonium hydroxide and sufficient saturated ammonium oxalate solution to precipitate all of the calcium present. Cool, dilute to 250 ml., mix and pass through a dry filter. Take a 50 ml. aliquot portion, evaporate nearly to dryness, add 1 ml. of 1:1 H_2SO_4, evaporate to dryness and ignite to remove ammonium salts as directed for Na_2SO_4 on page 878. Dissolve in water, acidify slightly with HCl, and determine potassium according to the Lindo-Gladding, page 871, or the Modified Chloroplatinate method, page 870.

Potash Salts (Muriate and Sulfate of Potash, Sulfate of Potash and Magnesia, and Kainite).—Dissolve 2.5 grams in distilled water and dilute to 250 ml. without the addition of ammonium hydroxide and ammonium oxalate. Take a 50 ml. aliquot portion, acidify slightly with hydrochloric acid and determine the potassium [7] by the Lindo-Gladding or the Modified Chloroplatinate method.

[6] Association of Official Agricultural Chemists, Methods of Analysis, 2 ed., 1925. Washington, D. C.

[7] With muriate of potash in the absence of sulfate the potassium may also be determined by the Chloroplatinate method, page 869, or by the Perchlorate method, page 871.

Organic Compounds.—When it is desired to determine the total amount of potassium in organic substances such as cottonseed meal, tobacco stems, etc., saturate 10 grams of the sample with concentrated sulfuric acid and ignite in a muffle at a low red heat to destroy organic matter. Add a little strong hydrochloric acid, warm slightly to loosen the mass from the dish, transfer to a 500 ml. volumetric flask with boiling water, add to the hot solution a slight excess of ammonium hydroxide and sufficient saturated ammonium oxalate solution to precipitate all of the calcium present, cool, dilute to 500 ml., mix and pass through a dry filter. Take a 50 ml. aliquot portion, evaporate nearly to dryness, add 1 ml. of 1:1 H_2SO_4, evaporate to dryness and ignite to remove ammonium salts as described for Na_2SO_4 on page 878. Dissolve in water, and finally determine the potassium in accordance with the Lindo-Gladding or the Modified Chloroplatinate method.

Ashes from Wood, Cotton Hulls, etc.—Boil 10 grams of the sample with 300 ml. of water for 30 minutes, add to the hot solution a slight excess of strong ammonium hydroxide and then sufficient saturated ammonium oxalate solution to precipitate all of the calcium present. Cool, dilute to 500 ml., mix, and pass through a dry filter. Take a 50 ml. aliquot portion, evaporate nearly to dryness, add 1 ml. 1–1 H_2SO_4, evaporate to dryness and ignite to remove ammonium salts as described for Na_2SO_4, page 878. Dissolve in water, and determine potassium by the Lindo-Gladding or Modified Chloroplatinate method.

Procedure for Saline Residues, Soluble Salts, Brines, etc.—In the case of water-soluble products, the convenience of the analyst usually determines the manner of preparing the solution. Usually it is preferable to weigh out a convenient sample, to make up the solution to definite volume, and to take an aliquot portion for each determination. As a general rule, a sample should be taken sufficient to give about a half gram of solids.

Procedure for Water.—Evaporate a 1 liter or larger sample depending on the quality of the water.

SEPARATIONS

In analytical procedures when both potassium and sodium are to be determined, the alkali metals are usually weighed as chlorides or sulfates after all other basic and acid radicals have been separated from them. Even when potassium alone is to be determined, a great many basic and acid radicals if present interfere and must first be removed. Detailed procedures for making these separations are indicated below.

SEPARATION FROM THE HEAVY METALS

The heavy metals are seldom to be found in solutions in which the determination of potassium and other alkalies is required. If these metals are present, however, they can be readily precipitated by means of hydrogen sulfide and ammonium sulfide and separated in the usual manner. The excess sulfide may be removed by acidifying slightly with hydrochloric acid and boiling followed by filtration.

SEPARATION FROM SILICA

Place the solution in a platinum [8] or pyrex glass dish, acidify slightly with hydrochloric acid, and evaporate on the steam bath until the odor of hydrochloric acid in the dry residue can no longer be detected. Break up the dry mass with a platinum [8] or glass rod, cool, moisten with a minimum amount of concentrated hydrochloric acid, dissolve in a small quantity of distilled water, filter and wash the residue free from chlorides with hot water. For accurate work the solution should be evaporated again with hydrochloric acid to remove any small amount of silica that still may be present.

SEPARATION FROM IRON, ALUMINUM, CHROMIUM, TITANIUM, URANIUM, PHOSPHORIC ACID, ETC.

If phosphoric acid is present in amounts insufficient to combine with all the iron, alumina, etc., or is absent altogether, heat the solution to boiling, add a few drops of nitric acid to oxidize the iron, add gradually an excess of ammonia, boil for a minute or so, allow the precipitate to settle, and filter. Wash the precipitate free from chlorides with hot water.

If phosphoric acid is present in the solution in excess of that required to combine with the iron, alumina, etc., heat the solution to boiling, oxidize with nitric acid, add a slight excess of ferric chloride solution, and precipitate with ammonia as described above.

When the precipitate is considerable, it should be dissolved in hydrochloric acid, and the precipitation repeated.

If chromates are present, they must first be reduced to the chromic salt. For this purpose, add 10 to 15 ml. of hydrochloric acid and a small amount of alcohol to the solution and heat on the steam bath or hot plate for a few minutes. Heat to boiling and precipitate with ammonia as directed above. The reduction may also be done by boiling with sulfurous acid.

SEPARATION FROM SULFATES

Precipitate the sulfate radical as $BaSO_4$ by the addition of a slight excess of barium chloride to the hot solution as directed on page 908 for the determination of SO_4. Remove the excess of barium by addition of ammonia and ammonium carbonate as directed for the separation of barium below.

The two operations may be combined as follows: Add a slight excess of barium chloride to the hot solution and boil for a few minutes. Then, without filtering off the $BaSO_4$, add an excess of ammonia and ammonium carbonate, allow the precipitate to settle, filter, and wash free from chloride.[9]

SEPARATION FROM BARIUM, CALCIUM AND STRONTIUM

To the not too concentrated solution, add a slight excess of ammonia and ammonium carbonate, heat to boiling, allow the precipitate to settle, filter and wash the residue a few times with hot water. Dissolve the precipitate,

[8] Platinum is preferable but pyrex glass will give satisfactory results except where the greatest possible accuracy is required.

[9] This procedure does not give faultless results as some of the potassium is carried down with the precipitate and lost.

which is likely to contain small amounts of the alkalies, in a little dilute hydrochloric acid, and repeat the precipitation with ammonia and ammonium carbonate. Filter and wash the residue. Evaporate the combined filtrates to dryness in a platinum[10] dish and ignite cautiously at a very faint red heat to remove ammonium salts. Dissolve the residue in a little water, add a few drops of ammonia, ammonium carbonate, and ammonium oxalate, and allow to stand for several hours in order to precipitate the last traces of the alkaline earths. Filter and wash the residue free from chloride with hot water.

SEPARATION FROM IRON, ALUMINUM, CHROMIUM, BARIUM, CALCIUM, STRONTIUM, PHOSPHATE, SULFATE, ETC., IN ONE OPERATION

To the hot solution add a slight excess of barium chloride and boil for a few minutes. Then, without filtering off the $BaSO_4$, add an excess of ammonia and ammonium carbonate, heat to boiling, and allow the precipitate to settle. Filter and wash free from chloride with hot water. After evaporating the filtrate to dryness, removing the ammonium salts by ignition, and dissolving the residue in a little water, precipitate the last trace of barium and calcium by addition of a few drops of ammonia, ammonium carbonate, and ammonium oxalate. By this procedure a small portion of the alkalies is retained by the precipitate and lost.

SEPARATION FROM BORIC ACID

Acidify the solution strongly with hydrochloric acid and evaporate to dryness. Stir up the residue with 15 to 20 ml. of pure methyl alcohol and cautiously evaporate on a steam bath at not too high a temperature. Moisten the residue with a drop or two of concentrated hydrochloric acid, add 15 ml. of methyl alcohol, and again take to dryness. Repeat the evaporation with methyl alcohol a third time. This should be ample for the complete removal of half a gram of B_2O_3.

SEPARATION FROM MAGNESIUM

8-hydroxyquinoline Method.[11]—Prepare a 5% solution of the reagent by dissolving 5 grams of 8-hydroxyquinoline, C_9H_6NOH, (M.P. 73–74° C.) in 100 ml. of 2 N acetic acid. For the separation adjust the magnesium content of the solution to about .05 gram or less of MgO per 100 ml. of solution and acidify very slightly with hydrochloric acid. Sufficient ammonium salts should be present to prevent the precipitation of magnesium hydroxide. Oxalates will do no harm. Heat the solution to between 60 and 70° C., and make distinctly alkaline with ammonia. The alkalinity must be sufficient to remain slightly in excess after the addition of the 8-hydroxyquinoline reagent. To the alkaline

[10] A porcelain dish may be used but greater care must be exercised in the ignition to avoid loss of the alkali metals by volatilization, and a small amount of silica may be dissolved from the dish.

[11] R. Berg, Z. Anal. Chem., 71, 23 (1927); Hahn & Viewig, Z. Anal. Chem., 71, 122 (1927).

solution maintained between 60 and 70° C. add slowly from a pipette with constant stirring a slight excess of 5% 8-hydroxyquinoline reagent (25 ml. of the reagent is ample for the precipitation of 0.1 gram MgO). The color of the supernatant liquor will be yellow when an excess of the reagent is present. Allow the precipitate to settle, filter, and wash with approximately 1–40 ammonia solution at a temperature between 60 and 70° C. Evaporate the filtrate to dryness in a platinum dish, ignite gently to expel ammonium salts, and determine the alkalies in the residue.

The magnesium precipitate may be dried at 130 to 150° C. and weighed as $Mg(C_9H_6NO)_2$. The weight of the precipitate $\times 0.0777 = Mg$; $\times 0.1291 = MgO$.

Mercuric Oxide Method.—After removing other bases and acids, evaporate the solution of the chlorides to dryness, expel ammonium chloride by gentle ignition, and dissolve the residue—except for the small amount of magnesium oxide present—by warming with a little water. Add an excess of mercuric oxide in the form of a thin paste prepared by shaking up freshly precipitated mercuric oxide in water. Evaporate the mixture to complete dryness on the steam bath with frequent stirring, dry thoroughly and ignite gently at first and then more strongly until all the mercuric chloride present has been volatilized. (Be careful not to inhale the fumes.) The whole of the unchanged mercuric oxide need not be expelled by ignition. Digest the residue, composed of the excess of mercuric oxide, the precipitated magnesium oxide, and the alkali chlorides, with a small quantity of hot water, filter rapidly, and wash with successive portions of hot water, first by decantation and then on the filter, but do not prolong the operation unnecessarily. If desired, determine the magnesium in the residue by expelling the mercuric oxide by ignition and weighing the magnesium oxide. Acidify the filtrate, which contains the alkalies, with hydrochloric acid, evaporate to dryness, ignite gently, cool and weigh. If the residue contains a small amount of magnesium, as it usually does, determine the magnesium in an aliquot and apply the necessary correction. The mercuric oxide should be tested for alkalies by volatilizing a portion and testing the residue.

Barium Hydroxide Method.—Evaporate the solution, which may contain chloride, sulfate, or nitrate, to dryness and gently ignite to remove ammonium salts. Warm the residue with a small amount of water and treat the hot neutral solution so obtained with barium hydroxide solution until no more precipitate is formed and barium hydroxide remains in slight excess. Boil, filter and wash the precipitate with hot water. If desired, determine the magnesium in the residue. Treat the filtrate, which contains the alkalies, barium and a trace of magnesium, with an excess of ammonia and ammonium carbonate to remove the barium. Acidify the filtrate with hydrochloric acid and evaporate to dryness, ignite and weigh. This residue will contain a small amount of magnesium which may be determined in an aliquot portion and a correction applied.

Ammonium Phosphate Method.—To the hot solution, add an excess of ammonia and ammonium chloride, and precipitate the magnesium by adding a slight excess of ammonium phosphate. Allow the mixture to stand an hour or so, filter and wash the residue with 2% ammonia solution. Expel most of the free ammonia from the filtrate by evaporation, acidify very slightly with hydrochloric acid, and add an excess of ferric chloride solution, which should

color the solution slightly yellow. Neutralize the solution with ammonium carbonate, heat to boiling, and filter off the basic ferric phosphate, washing the residue with hot water. Evaporate the filtrate to dryness, ignite to expel ammonium salts, and determine the alkalies in the residue. For accurate work the ferric phosphate precipitate should be dissolved in hydrochloric acid and the precipitation repeated.

SEPARATION FROM AMMONIUM SALTS

The separation of ammonia and ammonium salts from the alkali metals is effected by evaporating the sample to dryness in a platinum dish on the steam bath followed by gentle ignition until ammonia fumes have been completely expelled. Gentle ignition is carried out in the manner described for the determination of sodium as NaCl, page 877, or as Na_2SO_4, page 878.

SEPARATION FROM SODIUM AND LITHIUM

Sodium and lithium do not interfere in the determination of potassium in accordance with the methods described below. Hence for the determination of potassium methods for separating these elements are not required.

SEPARATION FROM RUBIDIUM AND CAESIUM

Rubidium and caesium are seldom present in more than traces in solutions in which the determination of potassium is required. When present, these rare elements will be precipitated as chloroplatinates or perchlorates, along with potassium in the methods described below. The best procedure is to weigh the three elements together as chloroplatinates or perchlorates, and then to separate and determine the rubidium and caesium in accordance with procedures given on pages 894 to 898, finally obtaining the potassium by difference.

SEPARATION FROM A LARGE AMOUNT OF SODIUM

In determining potassium in sodium chloride brines and certain other products, which contain a large amount of sodium and only a little potassium, it may be desirable to first concentrate the potassium by removal of a part of the sodium.

Procedure.—Place the aqueous solution in an Erlenmeyer flask, acidify slightly with hydrochloric acid, and evaporate until on cooling no salt separates out. Set the flask containing the cold solution in ice water and saturate the solution with hydrochloric acid gas, introduced through a wide delivery tube. This operation will require careful watching to prevent plugging of the delivery tube. When the solution is saturated with the gas wash the delivery tube and the inside of the flask into the solution, and stir to break up any lumps. Filter using gentle suction. Transfer the precipitate to the filter with ice-cold water saturated with HCl gas, and wash several times with small quantities of this liquid, sucking the filter dry after each application of the wash liquid. The potassium will be found in the filtrate along with some sodium and salts of

other metals originally present, and may be determined by one of the methods given below.

METHODS FOR DETERMINATION OF POTASSIUM

DETERMINATION AS POTASSIUM CHLORIDE OR POTASSIUM SULFATE

Potassium may be weighed as chloride or sulfate after separating all other constituents as described under separations, pages 864 to 868. The procedure is the same as that described for sodium given on pages 877 and 878. Observe, however, that the potassium salts are a little more volatile than the corresponding sodium salts, so that greater care must be taken not to lose potassium by volatilization.

$$KCl \times 0.5244 = K;\ \times 0.6317 = K_2O;\ \times 1.1687 = K_2SO_4.$$
$$K_2SO_4 \times 0.4487 = K;\ \times 0.5405 = K_2O;\ \times 0.8557 = KCl.$$

THE CHLOROPLATINATE METHOD

Application.—This method is applicable in the presence of the chlorides of sodium, lithium, magnesium, calcium and strontium.

Principle.—Potassium chloroplatinate is practically insoluble in strong alcohol while the other chloroplatinates are readily soluble.

Procedure.—Treat the aqueous solution of the alkali chlorides contained in a small glass or porcelain dish with slightly more than enough chloroplatinic acid to convert all the chlorides present into the corresponding chloroplatinates. The chloroplatinic acid solution should contain the equivalent of 1 gram of platinum in each 10 ml. Evaporate the solution on the steam bath to a syrupy consistence, i.e. until solidification occurs on cooling. Flood the cooled residue with a small quantity of alcohol of at least 80% strength, grind thoroughly with a pestle made by enlarging the end of a glass rod, and allow to stand one-half hour. Pour the liquid through a previously weighed filtering crucible, and before adding more alcohol rub up the residue again with the glass pestle. Now continue the washing by decantation with small portions of alcohol until the wash liquid becomes colorless. Transfer the precipitate to the crucible and wash two or three times with alcohol. Dry in an oven at 110° C. for one hour, cool in a desiccator, and weigh as K_2PtCl_6.

$$K_2PtCl_6 \times 0.1608 = K;\ \times 0.1937 = K_2O;\ \times 0.3067 = KCl;\ \text{and}\ \times 0.3584 = K_2SO_4.$$

Remarks.—This method is considered to be the most accurate known for the estimation of potassium. Care should be taken not to conduct the evaporation at too high a temperature nor let it go too far, as this may cause the forma-

tion of anhydrous sodium chloroplatinate, which dissolves slowly in alcohol. Too large a volume of alcohol for washing should be avoided, as K_2PtCl_6 is slightly soluble in alcohol, especially that of 80%. For this reason 95% alcohol is preferable for the washing.

Instead of using a filtering crucible, the precipitate may be filtered on paper, dried, washed through the filter with hot water into a weighed platinum dish, evaporated to dryness, dried at 110° C., and weighed as K_2PtCl_6.

THE MODIFIED CHLOROPLATINATE METHOD[12]

Application.—The method is applicable in the presence of chlorides, sulfates, phosphates, nitrates, carbonates, borates and silicates, salts of sodium, barium, calcium, strontium, magnesium, iron and alumina, and is especially suited for the estimation of potassium in salines, potassium salts, and fertilizers in which only the potassium is desired.

Principle.—On evaporating a solution containing potassium with a slight excess of chloroplatinic acid, the potassium is completely transformed into potassium chloroplatinate which is insoluble in strong alcohol, while any of the other chloroplatinates which may be formed are either dissolved or decomposed by alcohol, so that the excess of chloroplatinic acid may be readily removed. After dissolving the K_2PtCl_6 along with any other soluble salts contained in the residue in hot water, the platinum is precipitated from the solution by magnesium, and from the weight of platinum so obtained, the amount of potassium present is calculated.

Procedure.—To the solution slightly acidified with hydrochloric acid, add chloroplatinic acid solution slightly in excess of that necessary for the complete precipitation of the potassium present, and evaporate the solution on the steam bath to a syrupy consistency, i.e., until solidification occurs on cooling. Flood the cooled residue with a small quantity of alcohol of at least 80% strength, grind thoroughly with a pestle made by enlarging the end of a glass rod, and allow to stand one-half hour. The alcoholic solution should be colored if an excess of chloroplatinic acid has been used. Pour the liquid through a small filter, using suction if desired, and before adding more alcohol, rub up the residue again with the pestle. Now continue the washing by decantation with small portions of alcohol until the wash liquid becomes colorless. Three or four washings usually suffice. Transfer the precipitate to the filter and wash two or three times with alcohol.

Dissolve the precipitate of K_2PtCl_6 along with any other soluble salts present in hot water, washing it through the filter into a beaker of convenient size. To the hot solution add about 4 ml. of concentrated HCl and approximately 0.5 gram magnesium for every 0.2 gram potassium present. A lump of stick magnesium is preferable but magnesium ribbon pressed into the form of a ball and held at the bottom of the beaker with a glass rod with occasional stirring will give good results. When the action has practically ceased, add a few ml. of hydrochloric acid and allow the flocculent platinum to settle, preferably by allowing the beaker to set for an hour on the hot plate. The supernatant liquid should be perfectly clear and limpid like water if reduction

[12] Hicks, J. Ind. Eng. Chem., 5, 650 (1913).

is complete. To make sure, add more magnesium, in which case the solution will darken if reduction be incomplete. To the completely reduced solution, add concentrated hydrochloric acid, and boil to dissolve any basic salts, filter, wash thoroughly with hot water, ignite, and weigh as platinum.

$$Pt \times 0.4006 = K;\ \times 0.4825 = K_2O;\ \times 0.7638 = KCl.$$

Remarks.—If the solution contains very large amounts of iron, alumina, or silica, it is preferable to remove the greater part of these before proceeding to the determination of potassium. Care should be taken to insure the complete removal of the soluble chloroplatinates from the residue without the use of an excessive amount of alcohol, and also that the subsequent reduction of the potassium chloroplatinate with magnesium be complete.

LINDO-GLADDING METHOD [13]

Application.—This method is applicable in the presence of chlorides, sulfates, and phosphates of the alkalies and magnesium.

Principle.—The potassium is precipitated as K_2PtCl_6 and the soluble chloroplatinates removed by washing with 80% alcohol. The impurities in the precipitate are then washed out by a strong solution of ammonium chloride saturated with K_2PtCl_6 and the wash solution is removed by again washing with alcohol. The purified K_2PtCl_6 is finally dried and weighed.

Procedure.—To the solution, slightly acidified with hydrochloric acid, add an excess of chloroplatinic acid solution, and evaporate on the water bath to a thick paste, avoiding the absorption of ammonia. Treat the residue with 80% alcohol. Wash the precipitate thoroughly with 80% alcohol both by decantation and on the filter, continuing the washing after the filtrate is colorless. Wash finally with 10 ml. of ammonium chloride solution prepared as follows: Dissolve 100 grams of pure ammonium chloride in 500 ml. of water, add from 5 to 10 grams of potassium chloroplatinate (K_2PtCl_6) and shake at intervals for six to eight hours. Allow the mixture to settle over night and filter. Repeat the washing with successive portions of the ammonium chloride solution five or six times in order to remove the impurities from the precipitate. Wash again thoroughly with 80% alcohol, dry for 30 minutes at 100° C., cool in a desiccator and weigh as K_2PtCl_6. The precipitate should be perfectly soluble in water.

$$K_2PtCl_6 \times 0.1608 = K;\ \times 0.1937 = K_2O;\ \times 0.3067 = KCl;\ \text{and}\ \times 0.3584 = K_2SO_4.$$

THE PERCHLORATE METHOD [14]

Application.—This method is applicable in the presence of chlorides and nitrates of barium, calcium, magnesium and the alkali metals, and also in the presence of phosphates. Sulfates should not be present.

[13] Association of Official Agricultural Chemists, Methods of Analysis, 2 ed., 1925. Washington, D. C.

[14] Wense, Zeit. angew. Chem., 691 (1891); 233 (1892); Caspari, Zeit. angew. Chem., 68 (1893). The perchlorate method with n-butyl alcohol and ethyl acetate, as the wash liquid is described on page 884. G. F. Smith (J. Am. Chem. Soc., 45, 2072 (1923)) uses n-butyl alcohol as the wash liquid.

Principle.—The separation depends on the insolubility of potassium perchlorate, and the solubility of sodium and other perchlorates in 97% alcohol.

Procedure.—To the neutral or slightly acidified solution, add twice as much perchloric acid [15] as is required to convert all the bases present into perchlorates, and evaporate on the steam bath with stirring to a syrupy consistency. Add a little hot water and continue the evaporation with constant stirring until all the hydrochloric acid is expelled and heavy fumes of perchloric acid are given off. Avoid excessive loss of perchloric acid. Stir up the cooled mass thoroughly with 20 ml. of 97% alcohol to which 0.2% perchloric acid has been added, but avoid breaking up the potassium perchlorate crystals too finely or else they may pass through the filter. Allow the mixture to settle, and decant the alcohol off through a filtering crucible. Repeat the washing once by decantation and then warm to remove the alcohol. Dissolve the residue in hot water, add about a half gram of perchloric acid and evaporate again until fumes of perchloric acid are given off. Wash the residue once by decantation and then several times on the filter. Remove the adhering washliquid by washing with pure 97% alcohol, dry in an oven at 110 to 130° C. and finally heat in a muffle for 15 minutes at 350° C.[16] Cool in a desiccator and weigh as $KClO_4$.

$$KClO_4 \times 0.2822 = K;\ \times 0.3399 = K_2O;\ \times 0.5381 = KCl.$$

SHORT METHOD FOR POTASSIUM IN SILICATE ROCKS [17]

Application.—The method is applicable to silicate rocks and minerals which are decomposed by digestion with HF and H_2SO_4, where only potassium is to be determined and where extreme accuracy is not required.

Principle.—The mineral is decomposed by hydrofluoric and sulfuric acids, the excess of acids expelled by gentle ignition, and the residue dissolved in dilute hydrochloric acid. The solution thus obtained is evaporated to dryness in the presence of a slight excess of chloroplatinic acid. The residue is washed with 95% alcohol containing 20 ml. of concentrated hydrochloric acid in a liter in order to remove the excess of chloroplatinic acid and soluble chloroplatinates. It is then washed through the filter with hot water, the potassium chloroplatinate reduced to metallic platinum by means of magnesium, and the platinum weighed. From the weight of the platinum the weight of potassium is calculated.

Procedure.—Weigh out a half gram sample of the mineral which has been ground to pass a No. 200 sieve, place in a small platinum dish or a large platinum crucible, moisten with a few drops of water, and add about 10 ml. of hydrofluoric acid and the equivalent of about 1 ml. of concentrated sulfuric acid. Hold the dish with the tongs and heat it and its contents cautiously over the free flame until the mineral is broken up and apparently completely decomposed, which requires only a few minutes. Any dark color due to organic matter

[15] Use reagent grade 60% perchloric acid.

[16] A temperature of 350° C. is required for complete dehydration of $KClO_4$ which has been crystallized from aqueous solution. Smith and Ross, J. Am. Chem. Soc., 47, 774 and 1020 (1925).

[17] Hicks and Bailey, U. S. Geol. Survey Bull. 660, 51 (1917).

should be disregarded. Evaporate the solution on the steam bath to complete dryness, and during this operation agitate the solution occasionally by giving the dish a swirling motion with the tongs. This treatment is nearly always sufficient to decompose the mineral, but if decomposition seems incomplete add more hydrofluoric acid and evaporate a second time, agitating the mixture frequently. Heat the dish and its contents on a radiator to expel the excess of hydrofluoric and sulfuric acids. Finally ignite gently to make sure of the complete removal of ammonium salts and to destroy organic matter. This operation will also expel much of the sulfuric acid combined with the iron and aluminum, but care should be taken not to heat high enough to render the iron and aluminum insoluble in hydrochloric acid. Cover the residue with dilute hydrochloric acid, which must be free from ammonium salts, and digest on the steam bath until solution is complete, adding more water and acid if necessary. Flakes of organic matter may be neglected.

The solution of the completely decomposed mineral is now filtered into a small pyrex glass or porcelain evaporating dish, chloroplatinic acid slightly in excess of that necessary to combine with all of the potassium present is added, and the solution evaporated on the steam bath until nearly all the hydrochloric acid is removed and the mass solidifies on cooling. Cover the cold residue with an alcohol-acid solution prepared by adding 20 ml. of concentrated hydrochloric acid to 1 liter of 95% alcohol. Chloroplatinic acid and its soluble salts are likely to be occluded in the ferric sulfate and basic salts formed on evaporation, making their complete removal troublesome. The acid in the alcohol wash liquid tends to correct this difficulty by destroying the basic salts and changing a portion of the ferric sulfate into chloride, which is readily soluble in alcohol. If the residue is amorphous stir up the mixture gently with a glass rod made into a pestle and allow it to stand until it becomes crystalline, then grind up the residue thoroughly with the pestle and allow it to stand a half hour, or until it becomes quite crystalline. Decant the solution through a filter paper. Grind the residue thoroughly with the pestle, add 10 ml. of the alcohol-acid wash solution, stir thoroughly, allow the suspension to settle, and decant the solution through the paper. Continue the washing by decantation, using small portions of the alcohol-acid solution and thoroughly stirring up the residue after each treatment, until the excess of chloroplatinic acid has been completely removed, but be careful to keep the quantity of wash liquid around 75 ml.

Dissolve the residue, which consists of potassium chloroplatinate mixed with salts of iron, aluminum, calcium, sodium, and other metals, in hot water, and wash the solution through the filter into a convenient-size beaker. Acidify with hydrochloric acid, heat almost to boiling, and reduce the chloroplatinate to platinum by stirring the solution with magnesium. About 1 ml. of concentrated hydrochloric acid and 0.5 gram of magnesium should be added for each 0.2 gram of potassium present. A lump of stick magnesium is preferable, but a wad of magnesium ribbon held at the bottom of the beaker with a glass rod with occasional stirring will give good results. After the complete reduction of the platinum and the complete solution of the magnesium allow the mixture to stand on the hot plate for an hour or so. The platinum will coagulate on the bottom of the beaker, and the solution will become colorless and limpid like water. To make sure of complete reduction add more magnesium, when, if

reduction is incomplete, the solution will darken. Finally add strong hydrochloric acid, boil the solution, filter through paper, and wash thoroughly with hot water. The platinum is then ignited in a small porcelain crucible, cooled in a desiccator, and weighed.

$$Pt \times 0.4006 = K;\ \times 0.4825 = K_2O;\ \times 0.7638 = KCl.$$

OTHER METHODS

Among other methods which have been proposed and used for the determination of potassium, may be mentioned the cobaltinitrite method;[18] the bitartrate method;[19] the colorimetric method;[20] the spectroscopic method;[21] the chloronitrotoluenesulfonate method;[22] and the napthol yellow S method.[23]

[18] Addie and Wood, J. Chem. Soc., **77**, 1076 (1900); Drushel, Am. J. Sci. (4), **24**, 433 (1907); **26**, 329 and 555 (1908); Bowser, J. Am. Chem. Soc., **33**, 1752 (1911). U. S. Dept. Agri. Bull. Chem., Bull. 132, pp. 137, 152 and 159.
[19] Bayer, Chem. Ztg., **17**, 686 (1893).
[20] Cameron and Failyer, J. Am. Chem. Soc., **25**, 1063 (1903); Hill, J. Am. Chem. Soc., **25**, 990 (1903).
[21] Gooch and Hart, Am. J. Sci. (3), **24**, 448 (1891).
[22] 6-Chloro-5-nitro-m-toluene sulfonate. Davies and Davies, J. Chem. Soc., **123**, 2976 (1923).
[23] The potassium salt of 2,4-dinitro-1-napthol-7-sulfonic acid. Clark and Willits, Ind. Eng. Chem., Anal. Ed., **8**, 209 (1936).

SODIUM

Sodium, **Na**, *at.wt.* 22.997; *sp.gr.* 0.97; *m.p.* 97.5° C.; *b.p.* 880° C.; *oxides* Na_2O, Na_2O_2, Na_2O_3

OCCURRENCE

Sodium is an abundant element widely disseminated in nature constituting 2.75% of known terrestrial matter.[24] It is found in many rocks and minerals and is an important constituent of feldspar, of the nepheline group of silicates, of certain pyroxenes, and of many other minerals. It is abundant in rock salt and other saline residues, in ocean water and salt lakes, and is present in nearly all natural waters. Sodium nitrate occurs in Chile, sodium borate in California, and sodium sulfate in Western United States, Canada and Russia.

DETECTION OF SODIUM

Sodium is usually identified by the color which it imparts to the flame or by means of the spectroscope. The solution is prepared as directed below under Solution of Sample and is freed from all constituents other than the chlorides of magnesium and the alkalies according to the methods given under Separations. With exceedingly small amounts of sodium, it may be necessary to remove the magnesium also. After acidifying with hydrochloric acid, a drop of the solution is brought into the flame by means of a loop of platinum wire. In the presence of sodium, the flame assumes an intense yellow color, which is usually sufficient to identify the element. The results may be confirmed by examining the flame in the spectroscope, when the characteristic yellow sodium line will be prominent even in the presence of traces of sodium. The spectrum of sodium is shown on Plate II (p. 119). As a matter of fact, the ever-presence of the sodium line is a hindrance to the success of the method, but by observing the sudden change in the intensity of the line, little trouble will be experienced in detecting exceedingly small amounts of the metal.

In waters and soluble salts, it is usually sufficient to test directly the concentrated solution in the flame or spectroscope.

Precipitation of sodium as zinc, magnesium, cobalt[25] or nickel[26] uranyl acetate as described under direct determination of sodium on pages 878 to 881

[24] Clarke, F. W., U. S. Geol. Survey Bull. 770, p. 34 (1924).
[25] Caley, J. Am. Chem. Soc., 51, 1965 (1929).
[26] Felstein and Ward, Analyst, 56, 245 (1931).

is of value in identifying the element. Other reactions which may be utilized in the identification of sodium is by precipitation as pyroantimonate ($H_2Na_2Sb_2O_7 \cdot H_2O$) and as caesium sodium bismuth nitrate ($(Cs_2NaBi(NO_2)_6$. The filtrate from the determination of potassium as chloroplatinate (page 869) may be treated with formic acid and ammonia to remove platinum (page 881) and used for the detection of sodium.

ESTIMATION OF SODIUM

The estimation of sodium is required in the analysis of rocks, minerals, soils, waters, brines, saline residues, and many technical products. It is of particular importance in the analysis of glass and refractories.

SOLUTION OF SAMPLE

Solution of the sample is effected in the same manner as described for potassium, pages 863 and 864.

SEPARATIONS

Separations from all constituents except the alkali metals are made in the same manner as described for potassium, pages 864 to 868. Sodium is separated along with lithium from potassium, rubidium and caesium by the chloroplatinate and perchlorate method for potassium (pages 869 and 871) and by the n-butyl alcohol-ethyl acetate procedure, pages 884 to 886. The separation of sodium from lithium is accomplished by the methods for lithium, pages 889

to 891, and by precipitation as NaCl from a solution of the perchlorates in anhydrous n-butyl alcohol containing HCl, page 886.

SEPARATION OF SODIUM FROM LARGE AMOUNTS OF POTASSIUM

When the determination of a small amount of sodium in the presence of a large amount of potassium is required, it may be desired to first concentrate the sodium by removal of a part of the potassium. For this purpose proceed as directed for separating potassium from a large amount of sodium, page 868. The sodium will be found in the filtrate along with some potassium and salts of other metals originally present. Interfering substances are then separated as directed under Separations and the sodium determined by one of the methods given below.

METHODS FOR DETERMINATION OF SODIUM

DETERMINATION AS SODIUM CHLORIDE

Sodium is commonly weighed as NaCl when it is already present as such or after conversion of other forms into the chloride. In the case of salts of volatile acids, such as nitrates for instance, the transformation is made by evaporating the solution to dryness with hydrochloric acid repeatedly or until only the chloride remains. When the sodium is present as a salt of a non-volatile acid, the latter is removed and the transformation effected according to the methods under Separations.

Usually the solution in which sodium chloride is to be determined will contain ammonium salts from some previous operation. In such cases, proceed as follows: Evaporate the sodium chloride solution, which must contain no other non-volatile substance, in a platinum dish to complete dryness on the water bath. Cover the dish with a watch-glass, and cautiously dry the residue in an air bath at 110 to 130° C. Make sure that no loss of sodium chloride is sustained by decrepitation during drying and subsequent ignition. Heat the dish and contents over a free flame held in the hand and moved back and forth under the dish in order to remove ammonium salts. But to avoid loss of sodium chloride by volatilization, take care not to heat the dish to more than a faint redness in any one spot and not to raise the temperature of the salt above incipient fusion. Cool the residue, dissolve it in a little water, and filter from the carbonaceous matter into a weighed platinum dish. Acidify the filtrate with hydrochloric acid and evaporate it to dryness on the water or steam bath.[27] Dry the residue in an oven at 110 to 130° C., ignite cautiously over a free

[27] Addition of 10 ml. of concentrated hydrochloric acid at the point where the salt begins to separate out will tend to prevent subsequent decrepitation.

flame, taking the precautions mentioned above to prevent loss of sodium chloride, cool in a desiccator, and weigh as NaCl.

$$NaCl \times 0.3934 = Na; \times 0.5303 = Na_2O.$$

DETERMINATION AS SODIUM SULFATE

Sodium is often determined by weighing as Na_2SO_4 when it is present as such or after conversion of other forms into the sulfate. In the case of salts of volatile acids, the change into the sulfate is made by simply evaporating the solution with a slight excess of sulfuric acid. With salts of non-volatile acids, the transformation is effected according to the methods under Separations. When the sodium is present as an organic salt, the substance is moistened with concentrated sulfuric acid and carefully heated over a free flame until fumes cease to come off. The residue is dissolved in water and filtered from the carbonaceous matter.

As a rule the solution in which sodium sulfate is to be determined will contain an excess of sulfuric acid. In such cases, evaporate the solution to dryness in a weighed platinum dish, and cautiously ignite the dry residue until fumes cease to come off. Cool, add a lump of ammonium carbonate to the contents of the dish, and ignite a second time at dull red heat until no more fumes are given off. Cool in a desiccator and weigh as Na_2SO_4. Repeat the ignition with the addition of ammonium carbonate until a constant weight is obtained.

In case an excess of sulfuric acid is not present, evaporate the solution to dryness in a weighed platinum dish, ignite, cool in a desiccator and weigh as Na_2SO_4.

$$Na_2SO_4 \times 0.3238 = Na; \times 0.4364 = Na_2O; \times 0.8230 = NaCl.$$

DETERMINATION BY DIFFERENCE

Ordinarily sodium and potassium are weighed together as chlorides or sulfates as detailed above for sodium. Potassium is then determined by one of the methods given above, pages 869 to 872, and the value for sodium obtained by difference.

DETERMINATION AS SODIUM ZINC URANYL ACETATE[28]

Application.—The method is applicable to the determination of small amounts of sodium in the presence of moderate amounts of potassium, ammonium, magnesium, calcium and barium, and small amounts of lithium and strontium preferably as chlorides. Sulfates may be present if the solution does not contain calcium, barium or strontium.[29] Phosphates, silicates, oxalates, and tartrates interfere.

[28] Barber and Kolthoff, J. Am. Chem. Soc., 50, 1625 (1928).

[29] Usually the reagent will contain some sulfate so that if barium, calcium or strontium is present in the sodium solution, barium should be added to the reagent in quantity sufficient to remove the sulfate.

Principle.—Sodium is precipitated as sodium zinc uranyl acetate—$NaZn(UO_2)_3(C_2H_3O_2)_9 \cdot 6H_2O$—and weighed.

Special Reagents Required.—Weigh 77 grams of Crystallized Uranyl Acetate ($UO_2(C_2H_3O_2)_2 \cdot 2H_2O$) and transfer to a 600 ml. beaker. Add 13.3 ml. of glacial acetic acid and 410 ml. of distilled water. Warm to about 70° C. and stir until solution is complete (= Solution A).

Weigh 231 grams of crystallized zinc acetate ($Zn(C_2H_3O_2)_2 \cdot 3H_2O$) into a tared 600 ml. beaker. Add 6.6 ml. of glacial acetic acid, 262 ml. of distilled water, warm to 70° C. and stir until solution is complete (= Solution B).

Mix solutions A and B at about 70° C., cool to approximately 20° C., and allow to stand for 24 hours. Filter into a clean, dry glass bottle. The solution thus prepared is practically permanent, but filtration may be required from time to time as the reagent must be free from turbidity when used (= Zinc uranyl acetate solution).

Saturate 95% ethyl alcohol with sodium zinc uranyl acetate at 20° C. (= wash alcohol).

Procedure.—Prepare a solution of the sample as directed on page 876 and separate interfering substances as directed on page 876. If the solution contains more than 20 mg. NaCl or more than 50 mg. KCl dilute it to definite volume in a volumetric flask with water, and take an aliquot portion containing not more than the above amounts of NaCl and KCl. Place the neutral solution thus obtained in a small pyrex beaker and evaporate to a volume of about 1 ml. or as far as possible without the separation of salts. Add to the concentrated solution at least 10 ml. of the zinc uranyl acetate reagent for each ml. of the concentrated solution and stir thoroughly. Partly immerse the beaker containing the solution in a water bath at 20° C. (±1°), and stir occasionally for 30 to 45 minutes. Filter through a weighed filtering crucible, using gentle suction. Pass all of the solution through the filter and suck it dry. Wash the precipitate 5 to 10 times, successively with 2 ml. portions of the zinc uranyl acetate reagent, sucking the filter dry after each application of reagent. Then wash the precipitate five times with 2 ml. portions of 95% ethyl alcohol saturated with sodium zinc uranyl acetate at 20° C. Finally wash thoroughly with ether to remove the alcohol, and suck dry air through the filter to remove the ether. Wipe the crucible clean with a moist and then a dry towel. Place the crucible containing the precipitate in the balance case, which should preferably contain a desiccating agent, for 10 minutes and weigh as ($NaC_2H_3O_2 \cdot Zn(C_2H_3O_2)_2 \cdot 3UO_2(C_2H_3O_2)_2 \cdot 6H_2O$).

Weight of precipitate $\times 0.01495 = Na$; $\times 0.0202 = Na_2O$; $\times 0.0381 = NaCl$.

MAGNESIUM URANYL ACETATE METHOD FOR SODIUM [30]

Application.—This method is applicable in the presence of the chlorides of potassium, ammonium, calcium, magnesium, barium, strontium, iron, aluminum, chromium. Sulfate may be present when barium and strontium are absent and calcium and ammonium are low. Anions which precipitate uranium in acetic acid solution should be absent (See p. 878).

[30] Caley and Foulk, J. Am. Chem. Soc., 51, 1664 (1929); Barber and Kolthoff, J. Am. Chem. Soc., 51, 3233 (1929); Caley and Sickman, J. Am. Chem. Soc., 52, 4247 (1930); Caley, J. Am. Chem. Soc., 54, 432 (1932).

Principle.—Sodium is precipitated as sodium magnesium uranyl acetate ($NaC_2H_3O_2 \cdot Mg(C_2H_3O_2)_2 \cdot 3UO_2(C_2H_3O_2)_2 \cdot 6\frac{1}{2}H_2O$), dried and weighed.

Special Reagents Required.—Place 90 grams of uranium acetate ($UO_2(C_2H_3O_2)_2 \cdot 2H_2O$) and 60 ml. of glacial acetic acid in a 2-liter Erlenmeyer flask, and add sufficient distilled water to make 1 liter, measured by a mark on the side of the flask. Warm to 70° C. and stir until solution is complete (= Solution A).

Place 600 grams of magnesium acetate ($Mg(C_2H_3O_2)_2 \cdot 4H_2O$) and 60 ml. of glacial acetic acid in a 2-liter Erlenmeyer flask, and add sufficient distilled water to make 1 liter, measured by a mark on the side of the flask. Warm to 70° C. and stir until solution is complete (= Solution B).

Mix together solutions *A* and *B* at 70° C., and then cool to 20° C. Allow the solution to stand at this temperature for 2 hours or longer, filter through a dry paper into an amber-colored bottle, and preserve for use away from direct sunlight. If further precipitation occurs, the solution should be filtered again before it is used (= Magnesium uranyl acetate solution).

Saturate 95% ethyl alcohol at 29° C. with dry sodium magnesium uranyl acetate ($NaC_2H_3O_2 \cdot Mg(C_2H_3O_3)_2 \cdot UO_2(C_2H_3O_2)_2 \cdot 6\frac{1}{2}H_2O$) and filter (= Wash liquid).

Preparation of Test Sample.—Prepare a solution of the sample to be tested as directed on page 876, and separate interfering substances as directed on page 876, finally obtaining a neutral solution preferably in the form of chloride.

If the prepared solution contains more than 25 mg. of sodium (Na), dilute the solution to definite volume with distilled water in a volumetric flask, and take an aliquot portion containing 25 mg. of sodium or less.

Procedure.—Place the neutral solution containing the sodium, preferably as chloride, in an Erlenmeyer flask or beaker and evaporate to a volume of 5 ml. or less, but separation of salts should be avoided. Add rapidly 100 to 250 ml. of the magnesium uranyl acetate solution depending on the quantity of sodium present. Partially immerse the vessel containing the mixture in a water bath maintained at 20° C. (±1°) and stir vigorously for 30 to 45 minutes. Filter through a weighed filtering crucible using gentle suction, transferring the precipitate to the crucible by means of the magnesium uranyl acetate solution. Wash the precipitate with 5 ml. portions of the alcohol wash liquid, allowing the crucible to be sucked dry after each washing. Dry the crucible and contents in an oven at 105 to 110° C. for 30 minutes, cool in a desiccator, and weigh as sodium magnesium uranyl acetate ($NaC_2H_3O_2 \cdot Mg(C_2H_3O_2)_2 \cdot 3UO_2(C_2H_3O_2)_2 \cdot 6\frac{1}{2}H_2O$).

Weight of precipitate $\times 0.0153 = Na$; $\times 0.0206 = Na_2O$; $\times 0.0389 = NaCl$.

Remarks.—During filtration the solution should be continually agitated to prevent the crystalline precipitate from adhering to the sides of the vessel. The wash liquid should preferably be delivered from a graduated wash bottle having a fine tip. The end of the washing process is indicated by the wash liquid going through colorless. Ordinarily 30 to 50 ml. of wash liquid will be required. Frequently salts may be thrown out of solution in the filtrate by the alcohol, giving the appearance of the precipitate running through the filter.

When sodium is to be determined in the presence of large quantities of potassium as in commercial potassium chloride, the potassium may be first partly removed by the method given on page 877 or by the following method:

Dissolve 1 gram of the sample in 5 ml. of distilled water and add a hot solution containing 2 grams of ammonium perchlorate in 3 ml. of water and 25 ml. of 95% ethyl alcohol. Mix, cool to room temperature, filter, and wash the precipitate 5 times with 2 ml. portions of 95% alcohol. Evaporate the filtrate to dryness, take up the residue in 1 ml. of water, and follow the procedure outlined above. This method is applicable to caustic potash after neutralizing with hydrochloric acid.

When the sodium content of the sample is around 1 milligram or less it is preferable to reduce the volume of the solution to 1 or 2 ml. before adding the magnesium uranyl acetate solution, but in all cases care must be taken to avoid separation of salts.

Quantities of sodium up to 50 milligrams can be handled by the method but greater care is required than with the recommended quantity of 25 milligrams. The milliliters of reagent added should be at least 10 times the number of milligrams of sodium present, but in any case 100 milliliters of reagent should be used. An excess of reagent will do no harm.

DIRECT DETERMINATION OF SODIUM IN SILICATE MATERIALS

After silicate materials have been decomposed with hydrofluoric and sulfuric acids as described on pages 883 and 884, or by the J. Lawrence Smith method (page 882) sodium may be determined directly by either the zinc or magnesium uranyl acetate method as described above.

DETERMINATION OF SODIUM IN THE FILTRATE AFTER REMOVING POTASSIUM AS CHLOROPLATINATE

A direct determination of sodium may be made by removing the platinum from the filtrate obtained in the determination of potassium by the Chloroplatinate Method, page 869, and finally weighing the sodium as NaCl or Na_2SO_4.

Carefully transfer the filtrate obtained in the determination of potassium by the Chloroplatinate Method, page 869, to a small beaker of convenient size and evaporate on the water or steam bath to remove most of the alcohol. Dilute to about 100 to 200 ml. with water, depending on the amount of platinum present. Add 5 ml. of formic acid,[31] and boil until the solution turns brown and initial reduction of platinum is indicated. Then add a slight excess of ammonia and continue boiling for a few minutes. Allow the mixture to stand on the hot plate for the platinum to settle. Filter hot and wash free from chloride with hot water.

Evaporate the combined filtrate and washings to dryness on the water or steam bath and ignite gently to remove ammonium salts and organic matter. Dissolve in water, filter into a weighed platinum dish and determine the sodium as NaCl or as Na_2SO_4 as described on page 877 or 878.

Remarks.—The platinum may also be reduced with hydrogen in which case evaporation to remove ammonium salts and organic matter is not necessary.

[31] Chem. News, 75, 256 (1897). A test for non-volatile matter should be made on the formic acid and if necessary a correction made in the weight of NaCl or Na_2SO_4 obtained.

For this purpose the water solution is placed in a small Erlenmeyer flask fitted with a two-hole rubber stopper carrying an inlet and outlet tube. The solution is heated nearly to boiling and the flask is connected to a hydrogen generator. Hydrogen is run into the solution until all air is expelled and the solution is saturated. The outlet tube is then closed and the solution allowed to stand under slight pressure from the generator until the platinum is completely reduced. The flask is then disconnected, the excess hydrogen blown out of the flask, the solution filtered, evaporated, and the sodium finally weighed as $NaCl$ or Na_2SO_4.

OTHER METHODS FOR SODIUM

Direct determination of sodium as sodium caesium bismuth nitrate [32] is of interest. Indirect volumetric determination of sodium [33] after precipitation as the triple acetate (pages 878 and 879) has received considerable attention and is of interest particularly where exceedingly small quantities of sodium are involved.

DETERMINATION OF THE ALKALIES IN SILICATES BY THE J. LAWRENCE SMITH METHOD [34]

Principle.—By heating the substance with 1 part of ammonium chloride and 8 parts of calcium carbonate, and leaching the sintered mass with water, the alkalies are obtained in solution in the form of chlorides along with some calcium, while the remaining metals are for the most part left behind as insoluble oxides, and the silica is changed to calcium silicate.

Procedure.—Triturate 0.5 gram of the finely powdered mineral with an equal quantity of pure ammonium chloride in an agate mortar, add 3 grams of precipitated calcium carbonate [35] and mix intimately with the former. Transfer the mixture to a platinum crucible (preferably the J. Lawrence Smith alkali crucible), rinse the mortar with 1 gram of calcium carbonate and add to the contents of the crucible. Place the covered crucible in a slightly inclined position with the top protected from the heat of the flame. This can be done by setting the crucible in a hole in a cylinder of fire clay, as shown in Fig. 108. Gradually heat the crucible over a small flame until no more ammonia is evolved, but avoid heating sufficiently to cause the evolution of ammonium chloride. This should require about fifteen minutes. Then raise the temperature until finally the lower three-fourths (and no more) of the crucible is brought to a red heat, and maintain this temperature for one hour. Allow the crucible to cool and remove the sintered cake by gently tapping the inverted crucible. Should this not be possible, digest the mass a few minutes with

[32] Ball, J. Chem. Soc., 95, 2126 (1909); 97, 1408 (1910); 103, 2110 and 2130 (1913).

[33] Caley, J. Am. Chem. Soc., 52, 1349 (1930); Dobins and Byrd, J. Am. Chem. Soc., 53, 3288 (1931); Furman, Caley and Schoonover, J. Am. Chem. Soc., 54, 1344 (1932); Kolthoff and Lingane, J. Am. Chem. Soc., 55, 1871 (1933).

[34] Am. J. Sci. (3), 1, 269 (1871); Hillebrand, U. S. Geol. Survey Bull. 422, 171 (1910).

[35] Blank determinations should be run on the calcium carbonate, and corrections made for its alkali content.

water to soften the cake, and then wash it into a platinum dish.[36] Heat the covered dish with 50 to 75 ml. of water for half an hour, reduce the large particles to a fine powder by rubbing with a pestle in the dish, and decant the clear solution through a filter. Wash the residue four times by decantation, transfer to a filter, and wash with hot water until a few ml. of the washings give only a slight turbidity with silver nitrate. To make sure the decomposition of the mineral has been complete, treat the residue with hydrochloric acid. No trace of undecomposed mineral should remain undissolved.

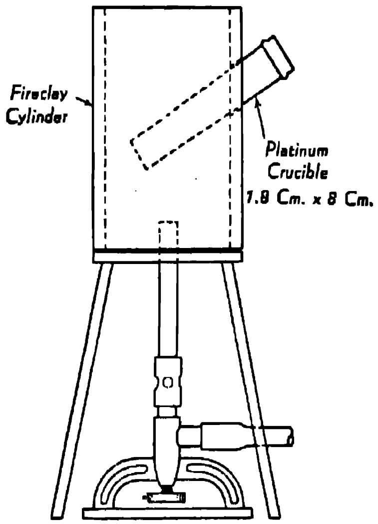


FIG. 108.

The aqueous extract obtained in the above operation contains the chlorides of calcium and the alkalies. To remove the calcium, treat the solution with ammonia and ammonium carbonate, heat to boiling, filter and wash the residue. As this precipitate invariably retains some alkali salts, it should be dissolved in hydrochloric acid and the precipitation repeated. Evaporate the filtrate to dryness in a platinum dish,[36] and expel the ammonium salts by gentle ignition over a moving flame. After cooling, dissolve the residue in a little water, and add a few drops of ammonia and ammonium oxalate to remove the last trace of calcium. After standing several hours, filter off the calcium oxalate, receive the filtrate in a weighed platinum dish, evaporate to dryness and ignite gently to remove ammonium salts. Moisten the cooled mass with hydrochloric acid to transform any carbonate into chloride, and again evaporate to dryness and ignite gently as described for NaCl, page 877. Cool in a desiccator and weigh the combined chlorides. Dissolve in water, and if an insoluble residue remains, filter off, weigh and deduct from the weight of the chlorides. Determine the potassium by one of the methods already described, pages 869 to 872, and obtain the value for sodium by difference.

DETERMINATION OF THE ALKALIES IN SILICATES BY THE HYDROFLUORIC ACID METHOD

Procedure.—Weigh out a half gram sample of the finely powdered mineral, place in a small platinum dish or a large platinum crucible, moisten with a few drops of water, and add about 10 ml. of concentrated hydrofluoric acid and 2 ml. of 1:3 sulfuric acid. Hold the dish with the tongs and heat it and its contents cautiously over the free flame for a few minutes. Evaporate the solution on the steam bath to complete dryness, and during this evaporation agitate the solution occasionally by giving the dish a swirling motion with the tongs. This treatment is nearly always sufficient to decompose the mineral, but if decomposition seems incomplete add more hydrofluoric acid and evaporate

[36] A Pyrex glass or porcelain dish may be used if platinum is not available.

a second time, agitating the mixture frequently. With refractory silicates it may be desirable to digest the mineral with the acid mixture in a covered crucible for an hour or so. Heat the dish and its contents on a radiator [37] to expel the excess of hydrofluoric and sulfuric acids. Cover the residue with dilute hydrochloric acid and digest on a steam bath until solution is complete, adding more water and acid if necessary. Flakes of organic matter which remain undissolved may be neglected. Remove the iron, alumina, calcium, magnesium, etc., by the methods described under Separations, pages 864 to 868. Finally weigh the sodium and potassium together as sulfates as described on page 878. Determine the potassium according to the modified chloroplatinate or Lindo-Gladding Method, pages 870 and 871, and obtain sodium by difference.

NOTE.—Following the decomposition of silicates by one of the above methods, sodium may be determined directly by the zinc or magnesium uranyl acetate method as indicated on page 878.

N-BUTYL ALCOHOL—ETHYL ACETATE METHOD FOR THE SEPARATION AND DETERMINATION OF THE ALKALIES [38]

Application.—This method is applicable in the presence of the chlorides of the alkali metals.

Principle.—The alkali metals are first obtained as chlorides free from all other constituents and are then converted into perchlorates. Sodium and lithium are dissolved out in a mixture of n-butyl alcohol and ethyl acetate, the mixture is filtered through a filtering crucible which leaves the perchlorates of potassium, rubidium, and caesium on the filter ready to be dried and weighed, and sodium and lithium in the filtrate. Sodium is precipitated by adding a solution of HCl gas in n-butyl alcohol, as NaCl, and weighed. Lithium is finally converted to Li_2SO_4 and weighed.

Special Reagents Required.—60% reagent grade perchloric acid containing not more than 0.1 mg. of non-volatile matter per ml.

Reagent grade, anhydrous n-butyl alcohol, with boiling range of 116–118° C. at 760 m.m. (d. 25°/4 .8065) preferably dried by refluxing over metallic calcium.

Reagent grade, anhydrous ethyl acetate, free from ethyl alcohol, with purity of 99.7 to 100%.

N-butyl alcohol containing 20% HCl prepared by passing dry HCl gas into the n-butyl alcohol to obtain a solution slightly stronger than required. The proper concentration is then obtained by dilution with n-butyl alcohol.

[37] Hillebrand, W. F., U. S. Geol. Survey Bull. 422, p. 31 (1910) (reprinted, 1916). A large porcelain crucible fitted with a triangle to support the crucible serves well as a radiator for this purpose.

[38] Willard and Smith, J. Am. Chem. Soc., 44, 2816 (1922); 45, 293 (1923); Smith, J. Am. Chem. Soc., 47, 762 (1925); Smith and Ross, J. Am. Chem. Soc., 47, 774 (1925).

N-butyl alcohol containing 6–7% HCl prepared by diluting 40 ml. of the 20% solution with 100 ml. of n-butyl alcohol.

Separation of Potassium, Rubidium and Caesium as Perchlorates.—Obtain the mixed chlorides of the alkali metals free from other constituents as directed under solution of sample (pages 863 to 864), and Separations (pages 864 to 869). Dissolve in a little water and transfer to a 150 ml. beaker. Add two or three times the equivalent quantity of pure 60% perchloric acid (not less than 1 ml. in any case), and carefully evaporate to complete dryness on the hot plate at not over 350° C. Expel any $HClO_4$ condensed on the side walls of the beaker by brushing with a free flame. Cool, dissolve in 5 ml. of water and repeat the evaporation on the hot plate.

Cool the beaker and contents to about 80° C., add 10 to 20 ml. of a mixture of equal parts by volume of n-butyl alcohol and ethyl acetate and digest near the boiling point for 2 or 3 minutes. Cool to room temperature, and decant the supernatant liquid through a crucible which has been previously ignited and weighed. Wash the residue three times by decantation with 5 ml. portions of the n-butyl alcohol-ethyl acetate mixture. Reserve the filtrate.

Dissolve the residue in the beaker in a minimum amount of hot water, and again evaporate to dryness. Cool, add 10 ml. of the n-butyl alcohol-ethyl acetate solvent, digest for 2 or 3 minutes near the boiling point, cool and filter through the original crucible. Transfer the precipitate to the crucible by means of the n-butyl alcohol-ethyl acetate reagent using a fine jet from a wash bottle, and finally wash 10 to 15 times with about 1 ml. portion of the reagent. Combine and reserve the filtrates and washings for the determination of lithium and sodium.

Dry the original beaker on the hot plate, and then brush any unremoved particles of perchlorate into the crucible containing the bulk of the precipitate. Dry the crucible and precipitate in an oven at 110° C. for a few minutes, and finally in a muffle at 350° C. for 15 minutes. Cool in a desiccator and weigh as $KClO_4$.

$$KClO_4 \times 0.2822 = K;\ \times 0.3399 = K_2O;\ \times 0.5381 = KCl.$$

The value for potassium thus found must be corrected for any rubidium and caesium present. The latter two elements may be determined as directed on page 894.

Determination of Sodium.—Place the combined filtrates and washings from the above operation in a 150 ml. beaker and evaporate on the hot plate to 20 ml. in order to remove the ethyl acetate. Cool to room temperature. Add from a burette dropwise with constant stirring 1.5 ml. of n-butyl alcohol containing 20% of HCl gas and then add rapidly 7 ml. more to form a 6% HCl solution. Heat to boiling over a wire gauze with a free flame to coagulate the NaCl. Cool, filter on a weighed filtering crucible, and wash 8 or 10 times with n-butyl alcohol containing 6 to 7% HCl gas, but keeping the wash liquid at a minimum. A rubber tipped glass rod may be used to transfer the precipitate to the crucible. Reserve the filtrate and washings for the determination of lithium.

Dry the crucible and NaCl in an oven at 250° C. for 1 hour and then ignite in a muffle at 600° C. for 5 to 8 minutes, or at a very dull red heat over a free flame as described on page 877. Cool in a desiccator and weigh as impure NaCl. Wash the precipitate through the filter with hot water, dry and ignite the

crucible and filter again, cool and weigh. The loss in weight represents pure NaCl.

To the weight of NaCl thus obtained there should be added 0.6 mg. for each 100 ml. of combined filtrate and washings, because of the slight solubility of the NaCl in the wash liquid.

Determination of Lithium.—To the combined filtrate and washings reserved above for the determination of lithium contained in a small beaker, add 1/3 their volume of water forming two layers. Cover with a watch glass supported on glass hooks and evaporate on the steam bath in such a way as to avoid any condensation on the upper part of the beaker, which may cause loss by creeping. At the end add 5 to 10 ml. of water to make the removal of organic matter more complete before the perchloric acid takes effect. At the appearance of a slight brown coloration, remove the watch glass supports and rest the watch glass directly on the beaker. Heat the covered beaker on a wire gauze with a free flame to fumes of perchloric acid. Remove any brown coloration adhering to the beaker by brushing with the free flame. In case the perchloric acid is not sufficient to oxidize the last trace of organic matter a few drops more should be added. When the brown color has been completely removed, add 0.5 ml. of concentrated sulfuric acid, replace the watch glass, and then fume off the acid on a hot plate or over a low flame on a wire gauze. Cool, add 5 to 10 ml. water and wash down the cover glass and inner walls of the beaker with water. Transfer to a platinum crucible which has been previously ignited and weighed with lid.

Evaporate the solution cautiously to dryness, cover the crucible, and heat preferably by a ring burner until every trace of acid is removed. Finally heat in a muffle at 600° C. or over a free flame at dull red heat as described on page 878 for 5 to 10 minutes. Repeat the ignition to constant weight. Cool in a desiccator and weigh as $Li_2SO_4+Na_2SO_4$.

To correct for the Na_2SO_4, deduct 0.7 mg. for each 100 ml. of combined filtrate and washings used in the determination and thus obtain the corrected weight of Li_2SO_4.

Corrected weight of $Li_2SO_4 \times 0.1262 = Li$; $\times 0.2717 = Li_2O$; $\times 0.7712 = LiCl$.

LITHIUM

Lithium, Li, *at.wt.* 6.94; *sp.gr.* 0.53; *m.p.* 186° C.; *b.p.* 1400° C.; *oxides* Li_2O, Li_2O_2

OCCURRENCE

Lithium is a comparatively rare element, although it is widely disseminated in nature, being found in nearly all igneous rocks and in many mineral springs. It is an important constituent of the minerals lepidolite, spodumene, petalite, amblogonite, triphylite, lithrophylite, and certain tourmalines. It frequently occurs in feldspar, muscovite and beryl.

DETECTION OF LITHIUM

Bring the sample into solution and separate the alkali chlorides from other constituents as directed on page 888. Digest the dry chlorides with amyl alcohol, with a mixture of absolute alcohol and ether or with n-butyl alcohol, filter, and evaporate the filtrate to dryness. Moisten the residue with dilute hydrochloric acid and examine it in the spectroscope. A bright red band and a faint orange line make up the flame spectrum of lithium, Plate II, page 119. These lie between the sodium line and the red potassium line and are easily recognized.

Lithium salts impart a carmine-red color to the flame, which is obscured by sodium, and by large amounts of potassium. But by the proper use of a color screen, the lithium flame may be recognized in the presence of large amounts of sodium.

Confirmation of the presence of lithium may be had by the formation of the sparingly soluble lithium phosphate, fluoride, acid aluminate or stearate.

ESTIMATION

The estimation of lithium may be required in the analysis of rocks, minerals, mineral waters, and certain technical and medicinal products such as glass, lithia waters, etc.

SOLUTION OF SAMPLE

Solution of the sample is prepared in the same manner as described for potassium, pages 863 to 864.

SEPARATIONS

Separations are made in the same manner as described for sodium, page 876. Sodium and potassium when present in large amounts may be partly removed by precipitation as described on page 868 and the lithium thereby concentrated.

METHODS FOR DETERMINATION OF LITHIUM

DETERMINATION AS LITHIUM CHLORIDE

Lithium may be weighed as LiCl. The procedure is practically the same as that described for sodium, page 877, but since lithium chloride is very hygroscopic, this salt must be weighed out of contact with the air. For this purpose the lithium chloride is ignited in a platinum crucible, cooled in a dessicator, and the crucible and contents weighed in a glass-stoppered weighing bottle.

$$LiCl \times 0.1637 = Li; \ \times 0.3524 = Li_2O; \ \times 1.2966 = Li_2SO_4.$$

DETERMINATION AS LITHIUM SULFATE

Lithium is weighed preferably as Li_2SO_4. The procedure is the same as that described for sodium, page 878; but since lithium bisulfate is easily broken up on heating, it is not necessary to ignite with ammonium carbonate.

$$Li_2SO_4 \times 0.1262 = Li; \ \times 0.2717 = Li_2O; \ \times 0.7712 = LiCl.$$

THE GOOCH METHOD [19]

Principle.—Lithium chloride is readily soluble in amyl alcohol, while sodium and potassium chlorides are not.

[19] Gooch, Proc. Am. Acad. Arts Sci., 22 (N. S. 14), 177 (1886); Am. Chem. J., 9, 33 (1887).

Procedure.—Prepare a solution and remove all constituents except the chlorides of the alkali metals as directed on page 888. Concentrate the solution as far as possible by evaporation, transfer it to a 50 ml. Erlenmeyer flask, add a small amount of amyl alcohol and heat cautiously on an asbestos plate until the water has been expelled and the boiling-point of the solution rises to about that of pure amyl alcohol (132° C.). To prevent bumping during this treatment, pass a current of dry air through the solution. When all of the water has been removed, the sodium and potassium chlorides, together with some LiOH will separate from the solution. Decant the solution through a filter and wash the residue several times with hot amyl alcohol. Moisten the residue with dilute hydrochloric acid, dissolve in a little water and repeat the extraction with amyl alcohol. If much lithium chloride is present, it will be necessary to repeat the extraction with amyl alcohol three or four times. Evaporate the combined filtrates and washings to dryness and dissolve in a little dilute sulfuric acid. Filter from the carbonaceous matter into a weighed platinum dish, evaporate to dryness, and remove the excess of sulfuric acid by gentle heating. Ignite the residue at dull redness, as described on page 888 for lithium sulfate, cool in a desiccator, and weigh as Li_2SO_4.

$$Li_2SO_4 \times 0.1262 = Li;\ \times 0.2717 = Li_2O;\ \times 0.7712 = LiCl.$$

Remarks.—For very accurate work, account must be taken of the fact that the lithium sulfate obtained according to the procedure just described always contains small amounts of potassium and sodium sulfates, if these metals were originally present. To correct for this, deduct 0.00041 gram for every 10 ml. of the filtrate exclusive of the washings in case only sodium chloride was present, or 0.00051 if only potassium chloride was present, and 0.00092 if both sodium and potassium chlorides were present.

THE RAMMELSBERG METHOD [40]

Principle.—Anhydrous lithium chloride is soluble in equal parts of alcohol and ether which have been saturated with hydrochloric acid gas, while the chlorides of sodium and potassium are practically insoluble in this mixture.

Procedure.—Prepare a solution and remove all constituents except the chlorides of the alkali metals as described on page 888. Evaporate the solution of the chlorides to dryness in a small flask provided with a two-hole stopper. During the evaporation, pass a current of dry air through the flask. Place the flask containing the dry residue in an oil or air bath and heat for half an hour at 140 to 150° C. during which time pass dry hydrochloric acid gas through the flask. Cool in a current of hydrochloric acid gas, treat the residue with a few ml. of absolute alcohol which has been saturated with hydrochloric acid gas, and add an equal volume of absolute ether. Close the flask tightly and allow it to stand with frequent shaking for twelve hours. Pour the solution through a filter, wet with the alcohol-ether mixture and wash the residue three times by decantation with the alcohol-ether mixture. Add a few more ml. of the alcohol-ether saturated with hydrochloric acid gas to the contents of the

[40] Rammelsberg, Pogg. Ann., 66, 79 (1845); Treadwell, Analytical Chemistry, 2, 55 (1911); John Wiley & Sons, New York.

flask and allow to stand again for twelve hours. Pour the liquid through a filter, and wash the residue by decantation with the alcohol-ether mixture until the residue tested in the spectroscope shows the complete absence of lithium. Carefully evaporate the combined alcohol-ether extract to dryness on a luke-warm water bath. Dissolve the residue in sufficient dilute sulfuric acid to convert all the lithium into the sulfate, transfer the solution to a weighed platinum dish, evaporate to dryness on the steam bath, and finally ignite carefully at dull red heat as described for lithium sulfate, page 888. Cool in a desiccator and weigh as Li_2SO_4.

$$Li_2SO_4 \times 0.1262 = Li; \times 0.2717 = Li_2O; \times 0.7712 = LiCl.$$

DETERMINATION OF LITHIUM BY THE ALCOHOL-ETHER PRECIPITATION METHOD [41]

Application.—This method is applicable to the chlorides of the alkali metals. The solution is prepared as directed on page 888 and is freed from all constituents except the chlorides of the alkali metals as directed under Separations, page 888, finally obtaining the dry mixed chlorides ignited and free from ammonia and organic matter, and accurately weighed. About 0.5 gram of mixed chloride should be used for the test.

Principle.—The chlorides of sodium and potassium are precipitated quantitatively from their concentrated solution while the lithium salt is soluble. The lithium chloride is converted to the sulfate and weighed.

Procedure.—The total alkali chlorides are dissolved in a minimum amount of cold water in a tall 200 ml. beaker. About 1.5 ml. will be more than sufficient for 0.5 gram of the salts. One drop of concentrated HCl is added and gradually 20 ml. absolute alcohol—the alcohol being dropped into the center of the beaker (not on the sides) while rotating the beaker. The sodium and potassium chlorides should be precipitated in a perfectly uniform granular condition. In a similar manner while rotating the beaker, 60 ml. of ether are added and the mixture is allowed to stand about 5 minutes, or until the precipitate is well agglomerated and the supernatant liquid almost clear. The beaker is rotated occasionally.

The mixture is then filtered through a weighed filtering crucible into an Erlenmeyer flask, using a bell-jar arrangement. The beaker is thoroughly washed with a mixture of 1 part of alcohol and 4 to 5 parts of ether. A rubber tipped rod is necessary for this purpose. The precipitate in the crucible is also well washed and the crucible set aside. The funnel is well washed in order to remove any lithium therefrom into the flask containing the filtrate.

The filtrate is evaporated to dryness on the water or steam bath (using a current of air). The residue is taken up with 10 ml. of absolute alcohol, warming if necessary, so that practically everything passes into solution. If a slight film remains on the bottom of the flask and sides, it is removed by rubbing with a rubber-tipped glass rod. While rotating the flask, 50 ml. of ether are added. One drop of concentrated HCl is added, the flask rotated and allowed to stand

[41] S. Palkin, J. Am. Chem. Soc., 38, 2331 (1916).

for one-half hour. It is well to rotate the flask at frequent intervals. When the fine precipitate has agglomerated (only a very small amount is usually precipitated), it is filtered through the same crucible as used in the first precipitation, into a tall beaker. The residue is washed with the ether-alcohol mixture, using the same precautions as outlined in the first precipitation. After drying in an oven, the crucible is gently ignited as directed on page 877 for sodium chloride, cooled, and weighed as $NaCl+KCl$.

The ether-alcohol solution of lithium is evaporated to dryness on the water or steam bath. The residue is taken up in a little water and a slight excess of sulfuric acid added. The solution is then carefully transferred to a weighed platinum dish, evaporated as far as possible on the steam bath, and the residue very gently ignited over a flame. By placing the dish on a triangle over an asbestos gauze and using a low flame, the solution can be evaporated without spattering.

Finally ignite at dull red heat as described for lithium sulfate, page 888, cool in a desiccator and weigh as Li_2SO_4.

$$Li_2SO_4 \times 0.1262 = Li; \ \times 0.2717 = Li_2O; \ \times 0.7712 = LiCl.$$

N-BUTYL ALCOHOL METHOD

This method involves the separation of lithium and sodium from potassium, rubidium and caesium, and then the separation of lithium from sodium. Lithium is finally weighed as Li_2SO_4. Details are given on pages 884 to 886.

SPECTROSCOPIC METHOD[42]

Dissolve the lithium salt containing small amounts of sodium and potassium resulting from the separation by the Gooch method, page 888, in 5 or 10 ml. of water, depending on the amount of lithium present. Gradually add measured amounts of this solution to a known volume of water—testing the solution from time to time in the spectroscope—until the lithium line appears. When only traces of lithium are present, it is better to dissolve the lithium salt in a little water and dilute to the vanishing point of the lithium line. Make the spectroscopic examination as follows: Prepare a loop by winding a platinum wire four times around a No. 10 wire. Plunge the loop into the solution, and remove with the axis parallel to the surface of the water. Evaporate the drop to dryness carefully, ignite in the Bunsen flame, and observe through a good spectroscope.

Before undertaking the determination, standardize the instrument and platinum loop by carrying out the determination with known amounts of lithium.

The method gives satisfactory results when only an approximation is desired. For weighable amounts of lithium one of the gravimetric methods for lithium given is preferable.

[42] Skinner and Collins, U. S. Dept. Agri. Bu. Chem., Bull. 153. A good bibliography is included in this bulletin.

OTHER METHODS FOR LITHIUM

Other methods which have been described for the determination of lithium include the acetone method,[43] iso-butyl alcohol method,[44] the pyridine method,[45] and the stearate method.[46]

[43] Brown and Reedy, Ind. Eng. Chem., Anal. Ed. 2, 304 (1930).
[44] Winkler, Z. Anal. Chem., 52, 628 (1913).
[45] Kahlenberg and Krauskopf, J. Am. Chem. Soc., 30, 1104 (1908).
[46] Caley, J. Am. Chem. Soc., 52, 2754 (1930).

RUBIDIUM AND CAESIUM

Rubidium, Rb, *at.wt.* 85.44; *sp.gr.* 1.53; *m.p.* 38.5° C.; *b.p.* 700° C.; *oxides* Rb_2O, Rb_2O_2, Rb_2O_4

Caesium, Cs, *at.wt.* 132.91; *sp.gr.* 1.90; *m.p.* 26° C.; *b.p.* 670° C.; *oxides* Cs_2O, Cs_2O_2, Cs_2O_4

OCCURRENCE

Rubidium is a rare element, found in lepidolite, in certain mineral springs, in the mother liquors from the potash works in Germany, in argols, and in the ashes of certain plants. It occurs in traces in the mineals leucite, spodumene, triphylite, petalite, carnallite, mica and orthoclase.

Caesium is the rarest of the alkali group of metals. It is an important constituent of the rare mineral pollucite, and occurs in some specimens of lepidolite and beryl, and in water from certain mineral springs.

DETECTION OF RUBIDIUM AND CAESIUM [47]

In the usual course of analysis these rare elements are brought into solution as described for potassium, pages 863 to 864, and separated along with sodium, potassium, and lithium in the form of chlorides from all other constituents as given under Separations, pages 864 to 869. Examination of the concentrated solution of these chlorides in the spectroscope will be sufficient to identify rubidium and caesium when these elements are present in appreciable amounts. Both elements have distinctly characteristic spectra as shown on Plate II, facing page 119.

Rubidium and caesium may be identified by following the quantitative procedure described on pages 894 to 898, first precipitating the rubidium and caesium as phosphomolybdates or as sodium bismuth nitrites and finally obtaining them as chloroplatinates. The presence of rubidium and caesium may be confirmed by dissolving this chloroplatinate precipitate in a little dilute HCl and examining the solution in the spectroscope.

[47] An excellent and precise method for the systematic qualitative separation and identification of the alkali metals is described by A. A. Noyes and W. C. Bray in "Qualitative Analysis for the Rarer Elements," 1927, The MacMillan Co.

Sodium and potassium when present in large amounts may be first partly removed in hydrochloric acid solution as described on page 868.

ESTIMATION OF RUBIDIUM AND CAESIUM

Estimation of these rare elements is seldom called for, but may sometimes be required in the analysis of rocks, minerals and mineral water. They have found some commercial application in the manufacture of photoelectric cells, and radio tubes and their estimation is of importance in this connection.

SOLUTION OF SAMPLE

Solution of the sample is effected in the same manner as described for potassium, pages 863 to 864.

SEPARATIONS

Rubidium and caesium are separated from all constituents except the chlorides of the alkali metals in accordance with procedures described for potassium, pages 864 to 869. They are separated from lithium and sodium by precipitation as chloroplatinates or perchlorates as described for potassium on pages 869, 870 and 884. They may be separated from potassium by the 9-phosphomolybdic acid method or the sodium bismuth nitrite method as described below.

SEPARATION FROM POTASSIUM BY 9-PHOSPHOMOLYBDIC ACID METHOD [48]

Special 9-Phosphomolybdic Acid Reagent (Luteo Acid).—Heat dodeca phosphomolybdic acid carefully to between 300 and 350° C. with continuous stirring to avoid local overheating. The color of the dry acid will turn from orange to

[48] O'Leary and Papish, Ind. Eng. Chem., Anal. Ed. 6, 110 (1934).

green and the above temperature is maintained until no orange particles remain. Cool and extract with distilled water. Oxidize the green solution so obtained with a little bromine water, and evaporate very slowly, when short, stout, yellow prisms of the luteo acid ($P_2O_5 \cdot 18MoO_3 \cdot 24\text{–}30H_2O$) will separate out. Filter off the luteo acid crystals, and dissolve in distilled water to form a 20% solution of the crystals for use as reagent.

Procedure.—After removing all other constituents as described under separations, except the chlorides or nitrates of potassium, rubidium and caesium, a sample is taken which contains not more than the equivalent of .08 gram rubidium chloride and about 1.0 gram potassium chloride. Evaporate the solution to dryness, and dissolve in 100 ml. of 1:3 nitric acid. Heat almost to boiling, and add with vigorous stirring an excess of the 20% solution of 9-phosphomolybdic acid crystals. The quantity of reagent required will be about 50 ml. for each gram of mixed chlorides present. Allow the mixture to settle on the steam bath at 40 to 60° C. for an hour, stir, and allow to settle for an hour longer at room temperature. Test a portion of the clear liquor with additional 9-phosphomolybdic acid reagent. Filter through a filtering crucible and wash with 1% sodium nitrate solution.

The filtrate contains all of the potassium along with excess reagent, sodium nitrate, and nitric acid. It may be discarded and the potassium obtained by difference as mentioned on page 868; or it may be treated with hydrogen sulfide to remove molybdenum as described below, and the potassium determined by one of the methods given on pages 869 to 872.

The precipitate contains all of the rubidium and caesium in the form of phosphomolybdates.

To remove the molybdenum proceed as follows: Dissolve the phosphomolybdate precipitate in a minimum quantity of 5% sodium hydroxide solution, saturate with hydrogen sulfide, heat to boiling, and just acidify with nitric acid. Boil to coagulate the precipitate, allow to settle, filter, wash, and discard the precipitate. This usually serves to remove all of the molybdenum. If the precipitation was incomplete, boil the filtrate to remove H_2S, add a slight excess of bromine water and boil to oxidize any molybdenum which may have been reduced, and repeat the precipitation with sulfide.

After the removal of molybdenum, evaporate the filtrate to about 20 ml., add 60 ml. of 95% alcohol, treat with a slight excess of chloroplatinic acid, and add a few ml. of ether. Allow the precipitate to settle, filter through a filtering crucible, and wash with 80% alcohol. The precipitate contains the chloroplatinates of rubidium and caesium along with a small quantity of sodium phosphate. The latter will do no harm in the subsequent separation and determination of rubidium and caesium.

To remove the platinum from the chloroplatinates, dissolve the precipitate in a little distilled water, add 3 drops of hydrazine hydrate and allow the reaction to proceed until vigorous evolution of gas ceases, which will cause the immediate precipitation of platinum. Filter off the precipitate and wash with distilled water. Cautiously add a few drops of aqua regia to the filtrate and boil for a short time to remove excess hydrazine.

The solution now contains rubidium and caesium chloride along with a little sodium phosphate and is ready for the separation and determination of rubidium and caesium by one of the methods given below.

Platinum may also be removed from the chloroplatinates by the method given on page 881 for the direct determination of sodium.

An alternative method for removing the phosphate radicle, after molybdenum has been separated from the 9-phosphomolybdate precipitate, is by treatment with ferric chloride and ammonia as described for potassium, page 865. In such a case ammonium salts would need to be subsequently removed by evaporation and ignition as described on page 868.

SEPARATION FROM POTASSIUM BY SODIUM BISMUTH NITRITE METHOD [49]

Special sodium bismuth nitrite reagent.—Dissolve 50 grams of reagent grade sodium nitrite ($NaNO_2$) in 100 ml. of distilled water, neutralize with a few drops of nitric acid, add 15 grams of reagent grade bismuth nitrate, $Bi(NO_3)_3 \cdot 5H_2O$, and shake until solution is complete. Filter the orange colored solution and preserve in a well stoppered bottle to prevent absorption of oxygen from the air. The solution should be fresh when used.

Procedure.—Prepare a solution and remove all constituents except the chlorides of the alkali metals as directed on page 895. Convert the mixed chlorides into nitrates by one evaporation with an excess of nitric acid. Dissolve the nitrate in as little water as possible, add 10 ml. of sodium bismuth nitrate reagent for each 1 ml. of sample, stir thoroughly and allow to stand for 24 hours in a 50 ml. Erlenmeyer flask well stoppered to prevent undue exposure to the air. Break up the precipitate thoroughly with a glass rod. Filter through a filtering crucible with a fairly thick asbestos felt using suction. At the same time transfer as much of the precipitate as possible to the crucible along with the liquid. By means of a rubber tipped glass rod and a portion of the filtrate transfer any remaining precipitate to the crucible. Wash the precipitate on the filter with 5 ml. of a 50:50 mixture of acetone and water and then complete the washing with pure acetone.

Dry the precipitate in an oven at 100° C. Then wash it through the filter into a small pyrex glass beaker with hot water. A little hydrochloric acid may be used if necessary. At the same time dissolve any residue remaining in the precipitation flask and add to the main solution. Evaporate to dryness with an excess of HCl to remove nitrates and nitrites. Dissolve in a little HCl and about 50 ml. of water and precipitate the bismuth with H_2S. Filter off the precipitate, wash and discard. Boil the filtrate to remove H_2S, and then separate and determine rubidium and caesium by one of the methods given below.

SEPARATION OF RUBIDIUM FROM CAESIUM AND SUBSEQUENT DETERMINATION OF THESE ELEMENTS

Methods for separating rubidium from caesium are only approximately quantitative. Probably the most satisfactory are the silico tungstic acid [50] and the antimony trichloride-ferric chloride [51] methods. Fortunately for the analyst, rubidium and caesium seldom occur together in appreciable amounts.

[49] Ball, J. Chem. Soc., 95, 2126 (1909); 97, 1408 (1910), 103, 2110 and 2130 (1913).
[50] O'Leary and Papish, Ind. Eng. Chem., Anal. Ed. 6, 110 (1934).
[51] Moses and Ritschel, Z. Anal. Chem., 70, 184 (1927).

Silico tungstic acid method.—After separating other constituents and obtaining a solution of the chlorides of rubidium and caesium as described above, evaporate the solution to small volume, add a little concentrated hydrochloric acid, and continue evaporation to dryness to insure complete removal of nitric acid. Take up in 50 to 75 ml. of 6 N hydrochloric acid and to the cold solution add 0.5 to 1.0 gram of solid silico tungstic acid dissolved in a few ml. of water. Allow the mixture to stand for 12 hours, filter through a filtering crucible and wash the precipitate with 6 N hydrochloric acid.

The filtrate contains all of the rubidium which may be determined as chloroplatinate by one of the methods, given on pages 869, 870 or 895, without removing the excess silico tungstic acid.

$$Rb_2PtCl_6 \times 0.2952 = Rb;\ \times 0.4177 = RbCl.$$
$$Pt \times 0.8753 = Rb;\ \times 1.2385 = RbCl.$$

Caesium is contained in the silico tungstic acid precipitate. Dissolve this precipitate in a minimum quantity of 5% sodium hydroxide solution, acidify faintly with nitric acid, and dilute to 200 ml. with distilled water. To the cold solution, add slowly with stirring a slight excess of 10% mercurous nitrate solution. The mercurous silico tungstate flocculates and settles rapidly. Filter, wash with 1% mercurous nitrate solution and discard the precipitate. Add a little aqua regia to the filtrate and boil to oxidize the mercury to the mercuric state. Determine caesium in this solution by one of the chloroplatinate methods given on pages 869, 870 or 895.

$$Cs_2PtCl_6 \times 0.3943 = Cs;\ \times 0.4996 = CsCl.$$
$$Pt \times 1.3605 = Cs;\ \times 1.7238 = CsCl.$$

Antimony Chloride-Ferric Chloride Method.[62]—After removing potassium by one of the methods given above, determine the rubidium and caesium as chloroplatinates as described for potassium, page 869.

$$Rb_2PtCl_6 \times 0.2952 = Rb;\ \times 0.4177 = RbCl.$$
$$Cs_2PtCl_6 \times 0.3943 = Cs;\ \times 0.4996 = CsCl.$$

If both rubidium and caesium are present their total weight as chloroplatinates will thus be obtained. The caesium is then separated by precipitation with antimony trichloride-ferric chloride and finally precipitated and weighed as perchlorate or chloroplatinate, and the rubidium is obtained by difference. The procedure is as follows:

Dissolve the chloroplatinates of rubidium and caesium obtained above in hot water, remove the platinum as described on page 881, and finally obtain the dry mixed chlorides in a small beaker. Add an equal weight of ferric chloride and dissolve in a minimum amount of water. For each gram of mixed chlorides present, add 50 ml. of glacial acetic acid. Heat to incipient boiling, add an equal volume of a cold 30% solution of antimony trichloride in glacial acetic acid and stir. The approximate composition of the precipitate is shown by the following formula:

$$4CsCl \cdot 4SbCl_3 \cdot FeCl_3.$$

[62] Moses and Ritschel, Z. Anal. Chem., **70**, 184 (1927).

Keep warm on the steam bath for an hour, and then allow to stand for 12 hours at room temperature. Filter through a filtering crucible, and wash with a 5% solution of antimony trichloride in glacial acetic acid.[53] Dissolve the precipitate in a little hydrochloric acid, washing it through the filter into a small beaker, and dilute with water until the acid concentration approximates 3 ml. of acid per 100 ml. of solution. Pass H_2S through the solution to precipitate the antimony, filter, wash, and discard the precipitate.

Boil the filtrate to remove H_2S, add a few drops of HNO_3 and boil to oxidize the iron, precipitate the iron with ammonia, evaporate and ignite gently to remove ammonium salts, page 877, and determine the caesium as perchlorate or chloroplatinate as described for potassium, pages 869 and 871. Rubidium is obtained by difference.

$$Cs_2PtCl_6 \times 0.3943 = Cs;\ \times 0.4996 = CsCl.$$
$$CsClO_4 \times 0.5718 = Cs;\ \times 0.7244 = CsCl.$$

When rubidium and caesium are present in very small amounts approximate determinations may be made by dissolving the chloroplatinate precipitate obtained on pages 895 and 897 in hot water and then following the spectroscopic method described for lithium, page 891.

[53] When rubidium is present in very large amounts, the precipitate must be dissolved in dilute hydrochloric acid and the operation repeated.

STRONTIUM [1]

Sr'', *at.wt.* 87.63; *sp.gr.* 2.6; *m.p.* 800° C.; *oxides* SrO and SrO_2

Strontium never occurs free in nature. It is found principally in the ores celestine, $SrSO_4$, and strontianite, $SrCO_3$. It generally accompanies calcium in the various forms of calcite and aragonite. It occurs with barium in barytocelestine, and is found in barytes. It also occurs associated with barium as a silicate in brewsterite, $Al_2O_3 \cdot H_4(BaSr)O_3 \cdot (SiO_2)_6 \cdot 3H_2O$. It is found in traces in certain mineral waters and in sea-water.

DETECTION

Strontium is precipitated with barium and calcium, in the filtrate from the ammonium sulfide group, by addition of ammonium carbonate to the ammoniacal solution. The precipitate is dissolved in acetic acid and treated with potassium dichromate, and the barium filtered off as $BaCrO_4$. Strontium and calcium in the filtrate are separated from the excess of potassium chromate by reprecipitation as carbonates by the addition of ammonium carbonate, the precipitate again dissolved in acetic acid and the excess of free acid neutralized with ammonia. Strontium may now be precipitated from the concentrated solution by boiling with an equal volume of a saturated solution of calcium sulfate.

Sodium Sulfate Test.—A saturated solution of the salt added to a solution containing strontium chloride, made strongly acid with acetic acid, and the mixture boiled, will produce a distinct precipitate if strontium exceeds 0.0015 normal. Calcium does not precipitate until 1.3 normality is reached.

Flame Test.—Strontium, preferably in the form of the chloride in a hydrochloric acid solution, placed on a platinum loop and held in a colorless flame, colors the flame crimson. (Lithium gives a red color, calcium a yellowish-red.) The test is best confirmed by means of the spectroscope.

The Spectra of Strongium.—Eight bright bands; 6 are red, 1 orange, 1 blue. Two of these, known as strontium β and γ, are red, the orange is strontium α and the blue strontium δ. The delicacy of the test is 0.6 milligram Sr per ml. The

[1] Strontium, the least abundant of the alkaline earth group, was discovered in the mineral strontianite found in strontian in Argyllshire by Cruikshank (1787). Davy isolated the metal (1807) by electrolysis of the chloride.

The compounds of strontium are used for medicinal purposes, for red fire in pyrotechnics; for the manufacture of iridescent glass; the dioxide for bleaching purposes; the sulfide for luminous paint; the hydroxide for refining of beet-root sugar, being preferable to lime, as the saccharate of strontia is more granular.

test is very much more delicate with the arc spectra, e.g., 0.03 milligram Sr per ml. See chapter on Barium, Preliminary Tests under Separations.

ESTIMATION

PREPARATION AND SOLUTION OF THE SAMPLE

The following facts regarding solubility may be of value in the determination of strontium. One hundred ml. of water dissolves 1.74 grams $Sr(OH)_2 \cdot H_2O$ at 20° C. The hydroxide is less soluble than that of barium. The peroxide dissolves to the extent of only 0.008 gram per 100 ml. 20° C. One hundred ml. of water dissolves 0.0011 gram,[2] $SrCO_3$ (18°); 0.0114 gram $SrSO_4$ at 18° and 0.0104 at 100°; the presence of sulfuric acid decreases this solubility, i.e., 0.00083 gram $SrSO_4$; 0.0051 gram $SrC_2O_4 \cdot H_2O$ at 18° and 5 grams at 100° C.: the presence of oxalic acid decreases this solubility. The sulfate dissolves in concentrated sulfuric acid, and is appreciably soluble in HCl, HNO_3, $HC_2H_3O_2$, NH_4Cl, NH_4NO_3, $NaCl$, $MgCl_2$. The carbonate and oxalate are soluble in mineral acids.

The procedure for the treatment of ores and strontium products is the same as those described for barium and calcium. We refer to the chapters on these elements for the preparation of the strontium solution.

In presence of sulfates, strontium may in part remain with silica, and if carbonates are present in the solution, due to contaminated ammonia, the strontium will precipitate with iron and aluminum, the same is true if phosphates are present, P_2O_5 being in excess of that which would combine with iron. In the ordinary scheme of analysis barium, strontium and calcium are determined in the filtrate from the ammonium sulfide group. The chemist is referred to the chapter on Barium for additional data on this group.

SEPARATIONS

Separation of Strontium from Magnesium and the Alkalies.—The procedure is the same as the one given in detail under barium for the separation of the alkaline earths from magnesium and the alkalies. Either the oxalic acid method or precipitation of strontium as a sulfate in presence of alcohol will accomplish this separation. If a sulfate precipitation is made it will be necessary to fuse the sulfate with sodium carbonate to get it into solution or to effect

[2] Treadwell claims solubility = 0.00055, i.e., 1 part $SrCO_3$ in 18,045 parts of water.

further separation from members of the ammonium carbonate group, should these be present.

Separation of Strontium from Calcium.[3]—Strontium and calcium are converted into the nitrates and taken to dryness and all water expelled by heating to 140° C. for an hour or more. The nitrates are now extracted with equal parts of absolute alcohol and anhydrous ether or by boiling with amyl alcohol at 130° C. (hood). Strontium remains insoluble and calcium goes into solution as the nitrate. Strontium nitrate may require further solution in water, evaporation to dryness, heating and extraction to remove calcium completely, should this be present in large excess. The nitrate of strontium is dissolved in water and strontium determined by one of the procedures given later. See detailed procedure for separation under Barium.

Separation of Strontium from Barium.—The procedure is given in detail under chapter on Barium. In brief one of the following methods may be used: Strontium and barium in a mixture of the nitrates are separated from calcium by treatment with ether-alcohol mixture, in which $Ba(NO_3)_2$ and $Sr(NO_3)_2$ are insoluble. The nitrates dissolved in water are separated by precipitating barium as $BaCrO_4$ from a faintly acetic acid solution, strontium remaining in solution.

If preferred, barium may be first removed as a chromate, strontium and calcium precipitated from an ammoniacal solution by $(NH_4)_2CO_3$ as carbonates, the carbonates converted to nitrates and $Sr(NO_3)_2$ separated from $Ca(NO_3)_2$ in an ether-alcohol solution or by amyl alcohol. Details of the separations are given under Barium.

GRAVIMETRIC METHODS

Strontium may be conveniently determined either as the sulfate, the carbonate or as the oxide. The first procedure is considered the best by authorities.

DETERMINATION AS STRONTIUM SULFATE, $SrSO_4$

Procedure.—A slight excess of dilute sulfuric acid is added to the neutral solution of strontium, and then an equal volume of alcohol. The mixture is stirred well and settled for several hours, or overnight, if more convenient. The precipitate, $SrSO_4$, is filtered onto a small ashless filter and washed first with 50% alcohol containing a little sulfuric acid, then with alcohol until free of acid. The precipitate is dried and the paper and the greater part of the salt ignited separately, then combined and weighed as $SrSO_4$.

Factors. $SrSO_4 \times 0.4770 = Sr$, or $\times 0.8038 = SrCO_3$, or $\times 0.5642 = SrO$.

[3] Advantage may be taken of the insolubility of strontium sulfate in ammonium sulfate in separating it from the soluble calcium salt.

DETERMINATION AS STRONTIUM CARBONATE

Strontium carbonate is not readily decomposed by ignition as is calcium carbonate, so that its determination in this form may be satisfactorily made.

Procedure.—The carbonate is precipitated by adding ammonium carbonate in slight excess [4] to the ammoniacal solution of strontium, heated nearly to boiling. The solution is allowed to stand for several hours and filtered cold. The washed strontium carbonate and filter are ignited gently and the cooled residue weighed as $SrCO_3$.

Factors. $SrCO_3 \times 0.5935 = Sr$, or $\times 1.2442 = SrSO_4$, or $\times 0.7019 = SrO$.

DETERMINATION AS OXIDE, SrO

Strontium is precipitated as the oxalate by addition of ammonium oxalate to the slightly ammoniacal solution. The precipitate is filtered and washed with water containing ammonium oxalate. The residue is ignited and weighed as SrO.

Factors. $SrO \times 0.8456 = Sr$, or $\times 1.7726 = SrSO_4$, or $\times 1.4247 = SrCO_3$.

VOLUMETRIC METHODS

The volumetric methods for determining strontium presuppose its isolation from other elements.

ALKALIMETRIC METHOD, TITRATION WITH STANDARD ACIDS

Either the carbonate or the oxide of strontium may be titrated with standard hydrochloric or nitric acids. The compound is treated with a known amount of standard acid added in excess, using methyl orange indicator. The solution is heated below boiling to complete the reaction and, upon cooling, the excess of acid is titrated with standard alkali.

One ml. normal acid = 0.04382 gram Sr, or 0.05182 gram SrO, or 0.07382 gram $SrCO_3$.

TITRATION OF THE CHLORIDE WITH SILVER NITRATE

Strontium chloride, free from other chlorides, may be determined indirectly by titration of its combined chlorine with silver nitrate by Mohr's method, using potassium chromate indicator. One ml. N $AgNO_3 = 0.04382$ gram Sr.

The oxide or carbonate is slightly supersaturated with hydrochloric, then taken to dryness and heated at 120° C. in the air bath to expel the excess of acid. Chlorine is determined on an aliquot portion.

[4] N.B. Avoid a large excess of $(NH_4)_2CO_3$. NH_4Cl has a solvent action on $SrCO_3$.

SULFUR [1]

S, *at.wt.* 32.06; *sp.gr.* 2.07; *m.p.* 112.8°; *b.p.* 444.6°; *oxides* S_2O_3, SO_2, SO_3, S_2O_7; *principal acids* $H_2S_2O_4$, H_2SO_3, H_2SO_4, $H_2S_2O_3$, *and* $H_2S_2O_8$

Sulfur occurs free in nature, generally mixed with earthy matter. The commercial product is exceedingly pure. The element occurs combined in sulfides—iron pyrites, FeS_2, ferro-ferri sulfide, $Fe_2O_3 \cdot 5FeS$; pyrrhotite, Fe_7S_8; copper pyrites, $CuFeS_2$; realgar, As_2S_2; orpiment, As_2S_3; galena, PbS; cinnabar, HgS; zinc blende, ZnS. Sulfate ores, gypsum, $CaSO_4 \cdot 2H_2O$, very abundant; barites or heavy spar, $BaSO_4$; celestite, $SrSO_4$; kieserite, $MgSO_4 \cdot H_2O$; epsom salts, $MgSO_4 \cdot 7H_2O$; glauber salt, $Na_2SO_4 \cdot 10H_2O$; sulfates of alkalies etc. In silicate and carbonate rocks it occurs generally as sulfide. It is found in gaseous form in H_2S and SO_2.

DETECTION

The following tests include the detection of free sulfur and its more important combined forms.

Element.—Sulfur is a polymorphous, yellow, brittle, odorless and tasteless solid; existing in the rhombic, monoclinic and triclinic crystalline forms, and also in an amorphous state. At 112° it melts to a pale yellow liquid; at 180° it thickens to a dark gum-like material, containing a large percentage of amorphous sulfur; at 260° it becomes a liquid again, and at 444.6° it boils, giving off a brownish-red vapor.

The important commercial forms of elemental sulfur are: **Flowers of Sulfur,** consisting of rhombic sulfur and not less than 30% of amorphous sulfur with a small amount of occluded free acid; **Powdered Sublimed Sulfur** (often called Flour Sulfur, a confusing term that should be abolished), consisting essentially of finely ground sublimed sulfur all in the rhombic form though at times a small percentage of amorphous sulfur is present; **Refined Brimstone** and **Roll Sulfur** (in some sections termed Virgin Lump Sulfur), consisting entirely of sublimed

[1] Sulfur was one of the earliest of chemical elements known to man. Mention is made of this in the records of the alchemists. The name of brimstone (burning stone) is of early origin. It is used in the manufacture of a large number of compounds including sulfuric acid. It finds uses in medicine, insecticides, manufacture of dyes, gunpowder, matches, rubber (vulcanization) and has more recently proven of value in improving highly alkaline soils. Sulfur compounds are extensively used in arts and sciences, in the home, in medicine, in the industries, in chemical manufacture, in agriculture, in the analytical laboratory.

sulfur in the rhombic form; **Powdered Brimstone** (often termed Commercial Flour, Superfine Flour and the like); and **Brimstone or Crude Lump Sulfur.** In these commercial sulfurs the physical form and the presence of certain small amounts of impurity are the characteristics of most importance as all the varieties named, even the Brimstones, usually contain in excess of 99.5% available sulfur.

Heated in the air sulfur burns with a blue flame, and is oxidized to SO_2, a gas with a characteristic pungent odor. This gas passed into a solution of potassium permanganate will decolorize it, if SO_2 is in excess of the amount that will react with the $KMnO_4$ in the solution.

If sulfur is dissolved in a hot alkali solution and a drop of this then placed on a silver coin, a stain of black Ag_2S will be evident, due to the action of the sulfur.

Sulfides.—Hydrogen sulfide, H_2S, is liberated when a sulfide is treated with a mineral acid. This gas blackens moist lead acetate paper. H_2S has a very disagreeable odor, which is characteristic.[2]

Sulfates.—A white compound, $BaSO_4$, is precipitated in presence of free hydrochloric acid when a solution of barium chloride is added to a solution of a sulphate.

Insoluble sulfates are decomposed by boiling or fusion with alkali carbonates, forming water-soluble alkali sulfates.

Sulfites.—Sulfur dioxide, SO_2, is evolved when a sulfite is treated with hydrochloric acid. The odor of the gas is characteristic.

Sulfur dioxide decolorizes a solution of potassium permanganate. (Use very dilute solution.)

Sulfites are distinguished from sulfates by their failure to form a white precipitate, when barium chloride is added to the solution acidified with hydrochloric acid; also by the fact that H_2S is formed when zinc is added to a solution of a sulfite, acidified by hydrochloric acid.

Thiosulfates.—Sulfur dioxide is evolved and free sulfur precipitated when a thiosulfate is acidified with dilute mineral acids. In presence of oxidizing agents sulfides will also liberate free sulfur.

Thiosulfates are strong reducing agents.

ESTIMATION

The determination of sulfur may be required in a great variety of substances, minerals, rocks, sulfur ores, acids, salts, water, gas, coal and other organic matter, insecticides, fungicides, stock medicants, fertilizer and other agricultural materials.

[2] E. C. Truesdale (Ind. Eng. Chem., Anal. Ed. 2, 299 (1930)) found that 1 part of H_2S in about 10 million of air can be detected by passing the gas through a capillary tip against a moist filter containing alkaline lead acetate reagent. A spot appeared corresponding to 1.5×10^{-9} gram H_2S.

The gravimetric determination of sulfur, by procedures of technical importance, depends upon its precipitation as barium sulfate, $BaSO_4$, after converting it into sulfuric acid, or a soluble sulfate, if not already in this form. Oxidation of free sulfur, sulfides, sulfites, metabisulfites, thiosulfates may be accomplished by either dry or by wet methods, details of which are given under subsequent procedures.

The volumetric methods of determining sulfur depend upon titration with oxidizing agents, or by acids, or by alkalies, according to the form of the sulfur compound, or by means of a substance forming an insoluble compound with sulfuric acid. For example sulfides are treated with a strong mineral acid (HCl), the evolved H_2S absorbed in a suitable reagent, and the sulfide formed is titrated with standard iodine. Sulfites may be determined either by oxidation with iodine or by titration with an acid in presence of methyl orange. Acid sulfites or metabistulfies may be determined by the iodine titration or by titration with an alkali in presence of phenolphthalein. Thiosulfates are titrated with iodine.

PREPARATION AND SOLUTION OF THE SAMPLE

In the preparation of the material for analysis, fine grinding is apt to oxidize sulfide sulfur [3] resulting in loss and lower percentage content. On the other hand contamination by sulfur from the flame during fusions must be guarded against. If a flame is used the crucible should be guarded by an asbestos shield as is shown in Fig. 112. The use of electric ovens avoids this contamination.

In presence of barium, lead, strontium and large amounts of calcium, the sulfur oxidized to sulfate will be found in part or in entirety combined with these in the silica residue after the acid attack and extraction. Fusion of this residue with sodium carbonate transposes the sulfate (and silica) to sodium salt which may now be leached out with water and separated from the water insoluble carbonates.

Loss of sulfide sulfur will occur if the ore is attacked by an acid without previous oxidation to sulfate form. The gravimetric method, which is preferred to volumetric methods, depends upon oxidation of the sulfur to sulfate form and precipitation as $BaSO_4$. Popoff and Neumann have shown that better crystals are formed and results are more accurate if the sulfate solution is added to the hot barium chloride reagent, acidified with HCl.[4] The presence of nitrates is objectionable.

Sulfide.—Sulfides of Na, K, Cs, Rb, Ca, Sr, Ba, Mg, Mn, Fe are soluble in dilute mineral acids. The sulfides of Ag, Hg, Pb, Cu, Bi, Cd, Co, Ni require strong acids for decomposition. These are also insoluble in sodium hydroxide and potassium hydroxide solutions. As, Sb and Sn sulfides are insoluble in dilute acids, but soluble in alkalies.

Sulfate.—With exception of $BaSO_4$, $CaSO_4$, $SrSO_4$ and $PbSO_4$, sulfates are soluble in water.

Thiosulfate.—Nearly all are soluble in water.

[3] E. T. Allen and J. Johnston, Ind. Eng. Chem., 2, 196 (1910).

[4] Stephen Popoff and E. W. Neumann, Ind. Eng. Chem., Anal. Ed. 2, 45 (1930).

Sulfite.—With exception of the sulfites of the alkalies, sulfites of the metals are difficultly soluble in water, but readily decomposed by acids.

DECOMPOSITION OF SULFUR ORES

The wet procedure for oxidation and decomposition of sulfur ores is given in detail under the Gravimetric Methods. This process is used for the valuation of the ore, and is applicable to a wide range of substances.

Fusion Method.—One gram of the finely ground ore (80 mesh) is intimately mixed with 6 grams of zinc oxide sodium carbonate mixture (4 parts $ZnO+1$ part Na_2CO_3), placing 2 grams more of the mixture over the charge. The material is fused and sulfur extracted according to the procedure described for coal—Eschka's method.

SULFUR IN COAL, ESCHKA'S METHOD

One gram of coal is intimately mixed with 3 grams of Eschka's compound, consisting of 2 parts of porous, calcined magnesia and 1 part of anhydrous sodium carbonate. The mixture, placed in a platinum crucible, is covered with about 2 grams more of Eschka's compound. The charge is placed in an open platinum crucible, which is protected from the flame by a shield, as shown in Fig. 113. If possible, a sulfur-free flame should be used to avoid contaminating the material. With proper precautions, the shield will prevent this. Heating in a crucible electric furnace completely avoids sulfur contamination. The mixture is heated very gradually, to drive off the volatile matter, the charge being stirred frequently with a platinum wire to allow free access of air. The heat is increased, after half an hour, to a dull redness. When the carbon has burned out, the gray color having changed to a yellow or light brown, the heat is removed and the crucible cooled.

The powdered fusion is digested with 100 ml. of hot water for half an hour, and the clear liquor decanted through a filter into a beaker. The residue is washed twice more with hot water, by decantation, and finally on the filter, until the volume of the total filtrate amounts to about 200 ml. About 5 ml. of bromine and a little hydrochloric acid are added, and the solution boiled. Sulfuric acid is now precipitated as $BaSO_4$ by addition of barium chloride to the hot solution, and sulfur determined by the first of the gravimetric procedures.

SULFUR IN ROCKS, SILICATES, AND INSOLUBLE SULFATES

The material in finely powdered form is fused in a large platinum crucible with about six times its weight of sodium carbonate (sulfur free) mixed with about 0.5 gram of potassium nitrate. The charge is protected from the flame by an asbestos board or silica plate with an opening to accommodate the crucible snugly, as shown in Fig. 113. The fusion is extracted with water, the filtrate evaporated to dryness and silica dehydrated. The residue is moistened with strong hydrochloric acid, then taken up with a little water, boiled free of CO_2, and silica filtered off. The filtrate contains the sulfate, which is now precipitated as barium sulfate according to one of the standard procedures.

Barium Sulfate.—This is transposed by fusion with sodium carbonate, as stated above. Barium carbonate remains in the water-insoluble residue. It is advisable to wash the residue in this case with hot sodium carbonate solution, to insure complete removal of the sodium sulfate. The filtrate is acidified with HCl, boiled free of CO_2 and $BaSO_4$, then precipitated.

Lead Sulfate.—This may be transposed by digesting the compound with a strong solution of sodium carbonate saturated with CO_2, keeping the solution at boiling temperature for half an hour or more. The sulfate will be in solution and the lead is precipitated as the water-insoluble carbonate.

Strontium or calcium sulfates may be transposed by the procedure described for lead.

SEPARATIONS

Substances Containing Iron

In precipitating barium sulfate, in presence of ferric salts, from hot solutions by the gravimetric procedure commonly followed, considerable iron is carried down by the precipitate. Since $Fe_2(SO_4)_3$ loses SO_3 upon ignition, and since Fe_2O_3 weighs much less than $BaSO_4$, low results will be obtained. Hence the removal of iron is necessary, or a method should be followed in which iron does not interfere. It is found that barium sulfate precipitated from a large volume of cold solution, in which the iron has been reduced to ferrous condition, is free from iron. Details of this procedure are given in the second of the gravimetric methods.

If sulfur is to be precipitated from hot solution of comparatively small volume (200 to 400 ml.), it is necessary to remove iron. This is accomplished by precipitating this as $Fe(OH)_3$ by addition of ammonium hydroxide in decided excess (5 to 10 ml. excess of strong NH_4OH, sp.gr. 0.90). If the solution is barely neutralized with ammonia, the iron hydroxide carries down considerable of the sulfate. Even with the precaution recommended some of the combined sulfuric acid is occluded by the precipitate, so that it is necessary to recover this by dissolving the precipitate with hydrochloric acid and reprecipitating the ferric hydroxide with an excess of ammonia. The combined filtrates are now treated with barium chloride, upon acidification with hydrochloric acid, according to the procedure first given.

Separation of Sulfur from Metals Forming an Insoluble Sulfate

This is accomplished by fusion of the compound with sodium carbonate and extraction of the mass with water. The metal remains with the residue and the sulfate of the alkali passes into solution. For details see subject under Preparation and Solution of the Sample.

Nitrates and Chlorates.—These are carried down with the precipitate as barium salts if they are present in appreciable amount. They may be removed from the solution by evaporation to dryness with hydrochloric acid.

Silica.—Silica will be carried down with the barium sulfate precipitate if present in appreciable amounts. It is removed by evaporation of the solution with hydrochloric acid, dehydrating the silicic acid, taking up with HCl and water and filtering.

Ammonium and Alkali Salts.—These have a negligible effect on the precipitate of $BaSO_4$ if this is precipitated from a large volume, according to the second gravimetric procedure. Their effect is evident when sulfur is determined in small volume.

GRAVIMETRIC DETERMINATION OF SULFUR

PRECIPITATION AS BARIUM SULFATE

The general laboratory procedure for precipitation of sulfate sulfur is to add to the solution diluted to 300–400 ml. and containing 4–8 ml. of 3 N HCl an excess of barium chloride reagent, the sulfur solution being previously heated to boiling. Popoff and Neuman have shown that the reverse order is preferable.[5] The procedure worked out in the laboratories of the General Chemical Company is to add the barium chloride reagent to the sulfate solution diluted to a large volume, the solution being at room temperature. The crystals of $BaSO_4$ thus obtained are comparatively large and are less apt to be contaminated. The three optional methods are given.

I. Precipitation of Barium Sulfate from Hot Solutions

Procedure.—The sulfur should be present in solution either as free sulfuric acid or as a sulfate salt. The solution is made acid by addition of hydrochloric acid (phenolphthalein indicator), and then 4 ml. added in excess (HCl, sp.gr. 1.2). After diluting to a volume of 400 ml. with hot water, the mixture is heated to boiling, and a 10% solution of barium chloride added in a fine stream,[6] through a funnel with a capillary stem, or from a burette, at the rate of 10 ml. in two to ten minutes. The reagent is added in slight excess of that required to react with the sulfuric acid or sulfate. (Ten ml. of 10% $BaCl_2 \cdot 2H_2O$ solution will precipitate about 0.13 g. of sulfur.) The beaker is placed on a steam bath and the precipitate allowed to settle for about an hour. The solution is filtered through a fine grade of filter paper (B. and A. grade A, or S. and S. grade No. 90), or through a tared Gooch crucible. Since the precipitate frequently passes through the filter it is advisable always to pass the solution through the same filter a second time. The precipitate is washed ten times with hot water, then dried, and ignited gently over a Bunsen burner, or in a muffle, for half an hour. (Blasting is not necessary, nor desirable.) The white $BaSO_4$ is cooled in a desiccator, and then weighed. If a filter paper has been used in place of a Gooch crucible, the ignition is best made in a porcelain cruci-

[5] S. Popoff and E. W. Neuman, Ind. Eng. Chem., Anal. Ed. 2, 45–54 (1930).

[6] E. Hintz and H. Weber recommend adding 100 ml. of N/10 $BaCl_2$ solution, boiling hot, to the hot sulfate solution all at once in place of slowly, as recommended in general practice. (See Treadwell and Hall, "Analytical Chemistry," 2, 3d Edition, p. 469.)

ble, with free access of air, the ignited sulfate, upon cooling, is brushed out of the crucible and so weighed.

Factors. $BaSO_4 \times 0.1373 = S$, or $\times 0.4202 = H_2SO_4$, or $\times 0.3766 = FeS$, or $\times 0.2744 = SO_2$, or $0.3430 = SO_3$, or $\times 0.4115 = SO_4$.

NOTE.—If much iron or alumina is present it is advisable to precipitate the sulfate from a large volume, by the second method, rather than attempt to remove these substances. If $BaSO_4$ is present in the original material its weight should be included with that of the precipitate.

II. Optional Method

Barium chloride solution (0.1 N) in sufficient quantity to completely precipitate the sulfur of the solution examined with about 5 ml. in excess, is acidified with 4–8 ml. of 3 N HCl and heated to boiling. The sulfate solution is now added, dropwise with constant stirring, and the resulting precipitate digested for 1 hour near the boiling point with occasional stirring. The precipitate is washed by decantation and on the filter with hot water until free of chlorides. (A Gooch crucible may be used.) The precipitate is ignited (800° C.) for an hour and weighed.

NOTE.—A final volume of 350 ml. with 0.8 gram of precipitate under the above conditions has proven to be highly satisfactory. The presence of KNO_3 and probably any nitrate is objectionable.[3]

III. Precipitation of Barium Sulfate from Cold Solutions—Large Volume

Introduction.—The method worked out by Allen and Bishop, General Chemical Company,[7] is especially adapted to the determination of sulfur in iron pyrites and materials high in sulfur, 30 to 50% sulfur, but by varying the amount of material used the range may be extended from smaller to greater amounts. The finely ground sample is oxidized by means of a mixture of bromine and potassium bromide followed by nitric acid. The nitric acid is expelled by evaporation to dryness, followed by a second evaporation with hydrochloric acid, which dehydrates the silica. Iron is now reduced to the ferrous condition and the silica and residue, undissolved by addition of hot water and HCl, is filtered off. The sulfur is precipitated in a large volume of cold solution, by barium chloride solution, as $BaSO_4$ and so weighed.

Reagents. ***Bromine—Potassium Bromide Solution.***—320 grams of potassium bromide are dissolved in just sufficient water to cause solution and mixed with 200 ml. of bromine, the bromine being poured into the saturated bromide solution. After mixing well the solution is diluted to 2000 ml.

Bromine—Carbon Tetrachloride Solution.—Carbon tetrachloride saturated with bromine.

Barium Chloride, anhydrous, 5% solution; or crystals, 6% solution.

Procedure. Preparation of Sample.—The sample ground to pass 80-mesh sieve is carefully mixed and quartered down to 10 grams. This is dried for one hour at 100° C. and then placed in a weighing tube.

[7] Paper before Eighth International Congress of Applied Chemistry: "An Exact Method for the Determination of Sulfur in Pyrites Ores," W. S. Allen and H. B. Bishop.

A factor weight, 1.373 grams of the sample, is placed in a deep beaker, 300 ml. capacity, 2½ by 4½ ins.

Oxidation of Sulfur.—Ten ml. of the bromine-potassium bromide mixture for pyrrhotite ore, or bromine—carbon tetrachloride reagent for pyrites ores, are added and the beaker covered with a dry watch-glass cover. After standing fifteen minutes in the cold bath (a casserole of water will do), with occasional shaking of the beaker, 15 ml. of concentrated nitric acid are added and the mixture allowed to stand fifteen minutes longer, at room temperature, and then warmed on an asbestos board on the steam bath until the reaction has apparently ceased and the bromine has been volatilized. The beaker is now placed within the ring of the steam bath so that the lower portion is exposed to steam heat. The solution is evaporated to dryness, the cover of the beaker being raised above the rim by means of riders (U-shaped glass rods), Fig. 109, 10 ml. of concentrated hydrochloric acid are now added and the solution again evaporated to dryness to expel the nitric acid. The silica is dehydrated by heating in the air oven at 100° C. for one hour, or overnight if preferred.

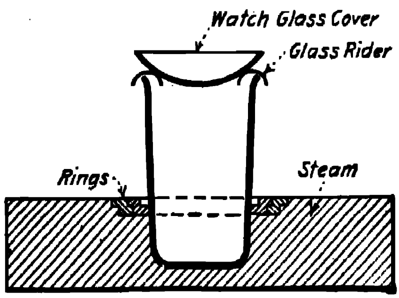


Fig. 109. Apparatus for Evaporator.

Reduction of Iron.—Four ml. of hydrochloric acid (sp.gr. 1.20), followed five minutes later by 100 ml. of hot water, are added, the sides of the beaker and the cover being rinsed into the solution. The riders being removed, the sample is gently boiled for five minutes to insure the solution of the sulfate. After cooling for about five minutes, approximately 0.2 gram powdered aluminum is stirred into the solution, keeping covered during the intervals between stirring. When the iron has been reduced, the solution becoming colorless, the sample is filtered into a 2500-ml. beaker, through a 12½ cm. filter paper. The beaker should be copped out and the residue on the filter washed nine times with hot water, filling the filter funnel and draining each time.

Precipitation of the Sulfur.—The solution in the large beaker is diluted to 1600 ml. with cold water and 6 ml. HCl (sp.gr. 1.20) added, and mixed by stirring. The barium chloride solution is now added by means of a special delivering cup (Figs. 109*a*–109*b*), which should drain at the rate of 5 ml. per minute. 125 ml. of barium chloride solution are added for ores containing 30 to 50% sulfur, the factor weight being taken. The solution is not stirred while the barium chloride is being added, but when the cup has drained, the solution is mixed by stirring. The $BaSO_4$ is allowed to settle, two or three hours being advisable, overnight being preferred.

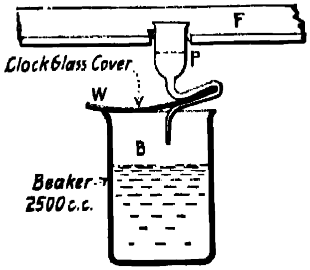


Fig. 109*a*.

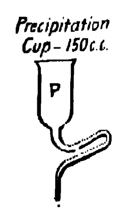


Fig. 109*b*.

Apparatus for Precipitating Sulfur.

Filtration.—The clear solution is filtered through a weighed Gooch crucible (35 ml.), using suction. This is best done by the automatic arrangement shown in Fig. 111. The beaker containing the solution is placed on a shelf; a siphon dipping to within half an inch of the precipitate at the bottom of the beaker is connected to the Gooch crucible by means of a tightly fitting stopper. The Gooch and thistle tube are best connected by heavy rubber tubing. The suction flask, or bottle, should have a capacity of about 3 liters. A Geissler stop-cock passes through the rubber stopper in the suction flask to relieve the pressure when the Gooch is to be removed. The precipitate is washed onto the asbestos mat in the crucible and washed with cold water six times, the beaker being copped out as usual.

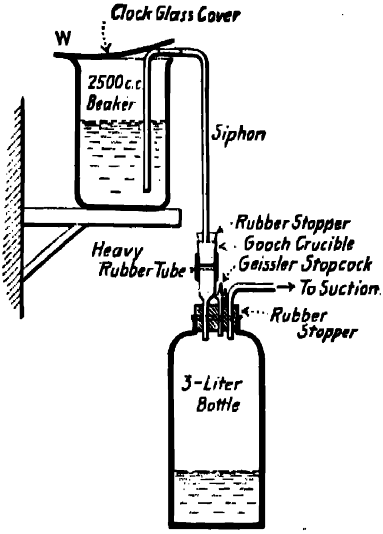


FIG. 110.—Apparatus for Filtering Barium Sulfate.

Ignition.—The precipitate is dried by placing the crucible on an asbestos board over a flame for twenty-five minutes and then heated over a direct flame for thirty minutes.

Calculation.—$BaSO_4 \times 10 = \%$ S. (If factor weight is taken.)

Factor. $BaSO_4 \times 0.1373 =$ gram S.

EVOLUTION METHOD FOR DETERMINING SULFUR IN IRON, STEEL, ORES, CINDERS, SULFIDES AND METALLURGICAL PRODUCTS

Introduction.—The method depends upon the fact that hydrogen sulfide is evolved when a sulfide is acted upon by a strong acid such as hydrochloric acid. This gas, absorbed by a suitable reagent, may be determined gravimetrically [8] by weighing directly the precipitated sulfide, or by oxidation of either the hydrogen sulfide evolved or the sulfide formed in the absorbing reagent, and precipitating sulfur as $BaSO_4$. It

[8] *Gravimetrically.* (a) Evolution of H_2S into solutions of $ZnCl_2$, KOH, $KMnO_4$, $AgNO_3$, $Hg(CN)_2$, H_2O_2, Br+HCl and subsequent oxidation to sulfate when necessary, and precipitation as $BaSO_4$. (b) Absorption of H_2S by neutral or alkaline solutions of lead, oxidation of PbS to $PbSO_4$ and weighing as such. (c) Absorption of H_2S in solutions of $AgNO_3$, $CdCl_2$, and weighing the precipitated sulfide.

may be determined volumetrically [9] by titrating the precipitated sulfide with iodine or by titrating the acid, formed by the reaction, with standard caustic. The iodine and caustic titrations may be made on the same run, or the sulfide may be weighed and the filtrate containing the free acid titrated, thus double checking results. The following reaction takes place when the gas is evolved and absorbed by neutral cadmium sulfate:

$$H_2S+CdSO_4=CdS \text{ precipitate}+H_2SO_4 \text{ free acid.}$$

The method is especially adapted to the determination of sulfur in iron and steel or in metallurgical products containing small amounts of sulfide. It may be applied to products containing larger amounts of sulfur as sulfides or sulfates, the latter condition requiring a special preliminary treatment.

The method is not applicable for determining free sulfur or sulfur in iron pyrites.

Reagents. *Iodine Solution.*—Two strengths of this reagent should be at hand for general work:

For iron and steel and low sulfur briquettes, etc. = .01 to 0.5% S......	.. N/30 I
For sulfur products containing over 0.5% S........................	.. N/10 I

Starch Solution.—Made from a good grade of soluble starch, 1 gram per 200 ml. of water. Fresh solutions are desirable, as the deteriorated material produces a greenish-brown color in place of the delicate blue desired. Flocks of insoluble starch will cause the same difficulty.

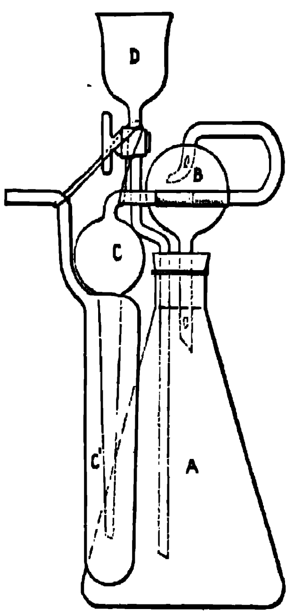


FIG. 111.—Scott's Apparatus for Determining Sulfur in Iron and Steel.

Cadmium Chloride or Cadmium Sulfate Solutions. Ammoniacal Solution.—Fifty-five grams of $CdCl_2 \cdot 2H_2O$ or 70 grams of the sulfate are dissolved in 500 ml. of distilled water. To this are added 1200 ml. NH_4OH (sp.gr. 0.90) and the solution diluted to 2500 ml. The solution is of such strength that 50 ml. will precipitate approximately 0.175 gram sulfur evolved as H_2S. This is equivalent to about 3.5% sulfur on a 5-gram sample.

Neutral Solution.—To be used where titration with caustic is desired. Seventy grams of $CdSO_4$ are dissolved in water and made up to 2500 ml. The solution should be neutral to methyl orange, otherwise add the requisite amount of H_2SO_4 or NaOH necessary, determined by titration of an aliquot portion.

Hydrochloric Acid.—One part concentrated acid to an equal volume of distilled water.

Sulfuric Acid.—One volume of concentrated acid to four volumes of distilled water.

Reducing Mixture for Reduction of Sulfates.—Five parts of $NaHCO_3$, 2 parts of C.P. aluminum powder and 1 part of pure carbon, best made by charring starch. A blank should be determined on this material and allowance made accordingly.

[9] *Volumetrically.* (*a*) Absorption in a solution of KOH, $CdCl_2$ or $CdSO_4$, $ZnCl_2$ or $ZnSO_4$, Na_2HAsO_3 and titration with iodine solution. (*b*) Absorption in iodized KI and titration of the excess of iodine with $Na_2S_2O_3$ solution. (*c*) Absorption in a neutral solution of a metallic salt and titration of the liberated acid. (*d*) Absorption in caustic alkali and addition to an acid solution of a reducible salt, e.g., Fe_2O_3 and titration of the lower oxide, FeO.

Stannous Chloride.—Ten per cent solution.

Fine Granular Aluminum or Zinc Metal.—Sulfur free, 20 mesh.

Apparatus.—The apparatus shown in the illustration, Fig. 111, is the authors' [10] modification of the form used as Baldwin Locomotive Works. This consists of an Erlenmeyer flask *A* of about 500-ml. capacity with large base. With material in which violent foaming occurs, during the evolution of hydrogen sulfide, it is advisable to use a wash bottle with large base, in preference to an Erlenmeyer flask. Through a rubber stopper is inserted a thistle tube with glass stop-cock *D*, by which the acid is introduced into the flask. The hydrogen sulfide passes through a potash connecting bulb with trap as shown. A hole blown in the side of the tube prevents liquid being swept through. Connected to the potash bulb is the absorption bulb *C*, which is suspended by a wire attached to the thistle tube. The apparatus is compact, so that on a large hot plate, 30 by 20 ins., a dozen outfits may readily be accommodated. With the use of this apparatus the writer has been able to make over seventy-five determinations of sulfur in steel in an ordinary day's run.

PREPARATION AND AMOUNT OF SAMPLE

The amount of material to be taken for the determination depends upon the sulfur content as shown by the following table:

Approximate % of sulfur present	Amount to take for analysis
0.01 to 1	5 grams
1.0 to 10	1
10.00 to 30	0.5
Above 30	0.25

The class of material will govern the method of procedure.

Iron and Steel.—A 5-gram sample of drillings or finely divided material is treated directly in the evolution flask with hydrochloric acid, 1 : 1, and the hydrogen sulfide absorbed in ammoniacal cadmium chloride. The sulfide formed is titrated with iodine.

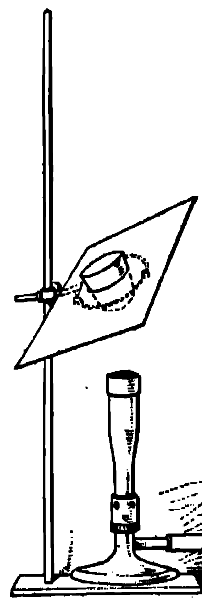


FIG. 112. Arrangement for protecting crucible from the flame.

Iron Ore Briquettes and Materials Containing Sulfates. Low Sulfur.—*Preliminary Reduction.* A 5-gram sample is intimately mixed with an equal weight of reducing mixture ($NaHCO_3+Al+C$) and wrapped in a 9-cm. ashless filter. The charge is placed in a 50-ml. nickel crucible with cover. The crucible is inserted half way into an asbestos board or perforated silica plate (see Fig. 112) and after covering, placed over a low flame of a Méker blast burner. The flame of the blast is gradually increased during the first five minutes and the charge blasted for about twenty minutes. The crucible will appear a bright red and carbon monoxide gas escaping from under the crucible lid will burn. The loss of sulfur, however, is not appreciable. The crucible

[10] W. W. Scott.

is cooled without removing the cover. When cold, the fused mass is quickly pulverized and placed in the dry evolution flask containing a mat of aluminum granules or C.P. zinc dust or granulated tin. Hydrogen sulfide is best evolved with hydrochloric acid to which 4 or 5 ml. of 10% stannous chloride has been added to reduce ferric iron. The gas is absorbed in ammonical cadmium chloride and the cadmium sulfide formed titrated with iodine.

Iron Sulfide for Available H_2S.—Since this product runs over 20% available hydrogen sulfide not over 0.5 gram sample should be taken. The H_2S is evolved by addition of dilute sulfuric acid, 1 : 4, in place of hydrochloric acid, and is absorbed by neutral cadmium sulfate. The acid formed by the reaction is titrated by standard N/10 NaOH.

Sodium Sulfide or Water-soluble Sulfides for Available H_2S.—Ten grams dissolved in water and diluted to 1000 ml.; 50 ml. = (0.5 gram) taken for analysis.

Details of Procedure

Evolution of Hydrogen Sulfide.—One-half to 1 gram of aluminum or zinc granules, 20 mesh, is placed over the bottom of the evolution flask and the sample placed above this mat of metal. The stopper with the thistle tube and condenser is inserted snugly into the neck of the flask. An absorption bulb containing about 20 ml. of distilled water is attached to the condenser. This bulb serves as a trap for the HCl that is driven out of the flask during the boiling. To this bulb is attached a second bulb containing 50 ml. of ammoniacal cadmium chloride. A third bulb may be attached if the sulfur content of the material examined is high; this, however, is seldom necessary when ammoniacal cadmium chloride is used. The rubber stopper and all rubber connections being air tight, 100 ml. of warm HCl, 1 : 1, is poured into the flask through the thistle tube, the stem of which should now dip well below the acid. The stopcock is closed during the violent action of the acid on the sample and opened when this has subsided. The acid trap prevents loss of H_2S through the thistle tube. The apparatus is now placed on the hot plate and the sample boiled vigorously for about twenty minutes. The flask is taken off the hot plate and the contents allowed to cool. At this stage it may be advisable to draw a current of air through the apparatus to sweep out any residual H_2S that may remain in the flask. Hydrogen gas is preferable to air.

Titration.—(*a*) The contents of the bulbs are poured into a 600-ml. beaker containing about 400 ml. of distilled water. The bulbs are washed out first with water and then with dilute acid. The excess of ammonia is neutralized with concentrated HCl, 5 ml. of starch solution added and the sulfide immediately titrated with standard iodine, additional hydrochloric acid being added from time to time during the titration to insure complete decomposition of the sulfide. The liquid appears yellowish red, orange, purplish red and finally a deep blue. Since the sulfide, when present in appreciable quantity, decomposes slowly, the solution should be strongly acid at the completion of the titration, and five minutes should be allowed for a permanent end-point.

Knowing the amount of iodine necessary, a check run may be made by adding to the neutral solution an excess of iodine followed by 5 ml. of starch solution and a large excess of concentrated hydrochloric acid. The excess of iodine is titrated with N/10 thiosulfate, $Na_2S_2O_3$, solution. (Arsenious acid will not do.) This procedure will prevent the loss of H_2S, which is apt to occur in samples high in sulfide.

(*b*) **An alternate method** is frequently advisable in high sulfurs. The precipitate is separated from the solution containing ammonia by filtration. The cadmium sulfide is now placed in the 600-ml. beaker with water and an excess of iodine run in. Starch is added, followed by hydrochloric acid. The excess of iodine is titrated with sodium thiosulfate, $Na_2S_2O_3$. By this method the heat action during the neutralization of ammonia is avoided and only the precipitate is titrated.

When the iodine titration exceeds 50 ml. of N/10 iodine, a smaller amount of the sample should be taken for analysis; the iodine titration for amounts of sulfur exceeding 0.1 gram is not satisfactory, owing to a fading end-point. The method for determining available hydrogen sulfide in high sulfide products, dealing with the titration of the free acid formed during the reaction, permits of larger samples being taken.

One ml. N/10 iodine = 0.001603 gram S.

Tenth Normal Equivalents

One ml. of N/10 iodine	= 0.001703 gram H_2S
" "	= 0.004395 gram FeS
" "	= 0.003903 gram Na_2S
" "	= 0.003607 gram CaS
" "	= 0.008471 gram BaS
" "	= 0.005661 gram Sb_2S_3
" "	= 0.011964 gram PbS
" "	= 0.011634 gram HgS
" "	= 0.004782 gram CuS
" "	= 0.007224 gram CdS
" "	= 0.004872 gram ZnS
" "	= 0.003269 gram Zn

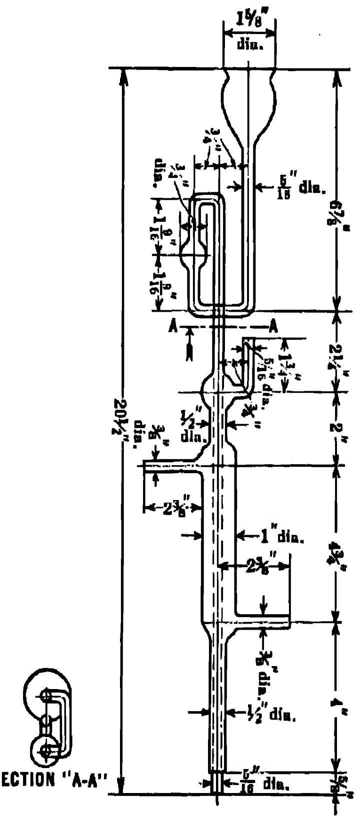


Fig. 113. Apparatus for Sulfur in Steel.

M. H. Steinmetz[11] makes use of a condenser so that all the hydrochloric acid and water vapors are returned to the flask while the non-condensable hydrogen sulfide passes over freely. In the final operation when the temperature is raised to produce boiling, no extra attention is necessary, thus simplifying the operation.

The condenser shown in Fig. 113 is connected to a Johnson sulfur flask by means of a sulfur-free rubber stopper. Connections are made to the condenser for the water circulation and also for the hydrogen sulfide gas, which is absorbed in a beaker containing the ammoniacal cadmium chloride solution. The test is started by adding 75 ml. hydrochloric (1 : 1) acid through the thistle tube. As soon as the violent action has ceased, heat may be applied rapidly until the sample is dissolved and the solution boils. The hydrogen sulfide gas evolved passes between the condenser walls and the tube delivering the acid into the flask.

Combustion Method for Evaluation of Sulfide Ores.—When a sulfide ore

[11] J. Ind. Eng. Chem., **20**, 983 (1928).

(pyrrhotite) is heated to redness in presence of oxygen both sulfur dioxide and trioxide are evolved. The first may be absorbed in suitable reagents and estimated volumetrically or gravimetrically. The trioxide mist is best retained by asbestos and weighed. The combustion furnace with silica tube used for determinations of carbon is adapted for sulfide ores. The finely powdered dry sample, spread in a thin layer in a 3-inch porcelain boat, is placed in the red hot tube and burned in a current of oxygen, which has been purified by passing through sodium hydroxide, concentrated sulfuric acid and phosphorus pentoxide. The trioxide mist is removed by passing the evolved gases through an asbestos filter (P_2O_5 bulb with asbestos in one arm adjacent to the combustion tube and P_2O_5 in the other). The SO_2 is absorbed in a mixture of bromine and nitric acid, and the sulfuric acid formed is titrated after removing the reagent by evaporation; or it is absorbed in an excess of standard iodine, the excess titrated with sodium arsenite or thiosulfate, and sulfur calculated. The iodine method is preferable to the bromine, as it is more rapid and the reagent less disagreeable to handle. The gravimetric method is the most reliable. The dioxide is absorbed in chromic acid (caustic will not give correct results owing to its affinity for carbon dioxide, a product of combustion of the free and combined carbon, that are generally present in sulfide ores. Pyrrhotite frequently contains as much as 1% carbon) and weighed. The combustion method cannot be recommended for extreme accuracy. The procedure may be used for the estimation of available sulfur, but does not give the total sulfur of the ore, since .2 to .5% remains in the cinder. Error may result from the following causes: (1) Incomplete combustion of the sulfur—due to sublimation of the sulfur to cooler zones of the combustion tube, and to a fine mist of sulfur passing unburned into the asbestos, where it is retained with SO_3 and weighed as such. (2) Error due to combined water of the ore. The results are apt to be .05 to 0.5% lower than those obtained by the barium sulfate procedures, the sulfur of the cinder being included with the available sulfur.

Notes and Precautions.—Although barium sulfate is only slightly soluble in water, it is appreciably soluble in the salts of the alkalies (Na, K and NH_4), and in a large excess of hydrochloric acid.

Barium sulfate occludes salts, especially nitrates and chlorides. Ferric chloride is carried down with this precipitate, though ferrous chloride is not; hence the reduction of iron is necessary. Occlusion of iron causes low results, as will be seen from the fact that with heating of $Fe_2(SO_4)_3$, SO_3 is volatilized, the salt decomposing to $Fe_2O_3+SO_3$. With the iron reduced the precipitate burns perfectly white, whereas with ferric iron present the precipitate is invariably red or yellow. Aluminum powder used by W. H. Seamon,[12] for reduction of iron in determination of sulfur, suggested its value in the method above given.

Potassium bromide is added to the bromine mix as a diluent to prevent too vigorous a reaction. Cooling the solution is for the same purpose as a loss of sulfur will result if the reaction is violent. This is especially the case in pyrrhotite ore.

Otto Folin[13] shows that precipitation of $BaSO_4$ in a large volume of cold solution produces large crystals.

Mechanical loss and reduction of $BaSO_4$ is avoided by the Gooch crucible.

Allen and Johnston have shown that the solubility of $BaSO_4$ varies directly with the acidity and the amount of wash water used.[14]

There is also a tendency of co-precipitation of $BaCl_2$ with $BaSO_4$. This is greater

[12] Chemical Engineer, September, 1908.

[13] Journal of Biological Chem., 1, 131–159 (1905).

[14] E. T. Allen and J. Johnston, J. Am. Chem. Soc., 32, 588 (1910).

when the sulfate is poured into the chloride than when the $BaCl_2$ is poured into the sulfate. The co-precipitation varies directly with the acidity, concentration of the SO_4 radical and rapidity of precipitation.

Potassium will contaminate the precipitate to a greater extent than will sodium.

DETERMINATION OF SULFATE IN CHROMIUM PLATING BATHS[15]

The chromic acid must be reduced to a chromic salt. Acetic acid is added to displace sulfate from its combination in the form of complex chromium ions. Either alcohol, hydroxylamine hydrochloride or concentrated hydrogen peroxide may be used as a reducing agent.

Procedure Using Alcohol as a Reducing Agent.—To 20 ml. of a 20 to 25% solution of chromic acid or 10 ml. of a 40% solution, diluted and filtered if necessary, add 15 to 20 ml. water, 7 ml. concentrated HCl, 25 ml. glacial acetic acid, 15 ml. alcohol and boil gently for 10 to 15 minutes (methyl alcohol may need a longer time). The solution should have a deep bluish green color free from brown or yellow tints, unless iron is present.

Dilute to 150 ml., heat to boiling, precipitate by the slow addition of 6 to 8 ml. of 10% $BaCl_2$, let stand hot at least one hour, filter, wash with water containing 1 ml. of concentrated HCl per 100 ml. to remove chromium salts, then with pure water ignite and weigh as $BaSO_4$. It should be white or at most faintly greenish. If yellowish it indicates contamination with $BaCrO_4$, due to incomplete reduction, or perhaps the presence of iron.

VOLUMETRIC METHODS FOR DETERMINING SOLUBLE SULFATES

Combined sulfuric acid in soluble sulfates is best determined gravimetrically; occasionally, however, a volumetric procedure is of technical value. A number of volumetric methods are based on the insolubility of barium sulfate. Two general procedures deserve mention: addition of barium chloride in known amount in slight excess of that required by the sulfate, and titrating the excess either with a soluble carbonate or a chromate; or addition of barium chromate and titrating the alkali chromate formed by the reaction. The sulfate is also determined by precipitation with a weak organic base benzidine, added in form of the hydrochloride salt; the benzidine sulfate, filtered off, is titrated with caustic. The typical procedures given below will meet general requirements for the volumetric determination of sulfates.

[15] H. H. Willard and R. Schneidewind, Trans. Electro-Chem. Soc., 46, 333–349 (1929).

DETERMINATION OF SULFUR BY TITRATION WITH BARIUM CHLORIDE AND POTASSIUM CHROMATE—WIDENSTEIN'S METHOD MODIFIED[16]

Reaction.—

$$Na_2SO_4+BaCl_2=BaSO_4+2NaCl \text{ and excess } BaCl_2+K_2CrO_4=BaCrO_4+2KCl.$$

Procedure.—The substance containing the sulfate in solution is diluted to 50 ml. in a small flask, acidified with hydrochloric acid, if necessary, heated to boiling, and precipitated with a slight excess of N/4 barium chloride added from a burette (1 ml. $BaCl_2=0.01$ gram SO_3). The precipitate settles rapidly, so that a large excess of the reagent may readily be avoided. The mixture is cautiously neutralized with ammonia, free from carbonate (CO_2 may be precipitated with $CaCl_2$ solution), the solution heated to boiling, and N/4 potassium chromate added from a burette in .5 ml. portions, each time removing the flask from the heat, allowing the precipitate to settle and examining the clear solution. A faint yellow color will appear as soon as the excess of barium has been precipitated and a few drops of the chromate in excess are present in the solution. The value of the chromate being equivalent to the barium chloride ml. per ml., the difference between the two titrations is due to the barium chloride required by the sulfate.

$$\text{One ml. N/4 } BaCl_2=0.01001 \text{ gram } SO_3.$$

NOTES.—Salts of the alkalies, alkaline earths (Sr and Ca) and zinc and cadmium do not interfere. Nickel, cobalt and copper, however, give colored solutions which prevent the yellow chromate being seen. Should the latter be present, the end-point may be recognized by using ammoniacal lead acetate as an outside indicator (1 vol. NH_4OH+4 vols. $PbC_2H_3O_2 \cdot 3H_2O$, 5% sol.), the indicator and titrated solution being mixed drop per drop on a white tile. A yellowish red color indicates the presence of chromate.

H. Roth[17] has shown the use of a test paper containing p_1p_2 diamino diphenyl amine ($NH_2C_6H_4NHC_6H_4NH_2$) indicator as a delicate test for chromate. The paper, a pale gray color when treated with the compound, is kept in a closed, opaque container. When a drop of solution containing a trace of chromate is placed on the paper a blue colored spot is obtained. In the volumetric determination of sulfates, by addition of an excess of $BaCl_2$ solution and determining the excess of Ba by precipitation with a chromate or dichromate, the exact point may be determined by spot tests with the indicator paper, the slightest excess of chromate being detected.

[16] See "Volumetric Analysis," Sutton, 10th Ed., p. 350.
[17] Z. angew. Chem., 39, 1599 (1926).

A. PRECIPITATION OF THE SULFATE WITH BARIUM CHROMATE AND TITRATION OF EQUIVALENT, LIBERATED CHROMATE WITH IODINE AND THIOSULFATE, HINMAN'S METHOD[18]

The sulfate, precipitated by barium chromate, liberates an equivalent amount of chromic acid, which is determined by treating with potassium iodide and titrating the liberated iodine with thiosulfate.

Reactions.—$Na_2SO_4+BaCrO_4=BaSO_4+Na_2CrO_4$,

$$Na_2CrO_4+3KI+8HCl=2NaCl+3KCl+CrCl_3+4H_2O+3I,$$
$$2Na_2S_2O_3+I_2=2NaI+Na_2S_4O_6.$$

Procedure.[19]—The solution of the sulfate, containing not over 2% of SO_3, if acid, is almost neutralized with potassium hydroxide, then heated to boiling, and an excess of barium chromate solution added.[20] After boiling for one to five minutes, the hot solution is neutralized by adding calcium carbonate[21] until no further effervescence occurs. The precipitate is filtered off and washed with hot water. The combined filtrates containing the chromate liberated by the sulfate through double decomposition, is acidified with 5 ml. concentrated hydrochloric acid per each 100 ml. of filtrate and an excess of potassium iodide added. Iodine equivalent to the chromic acid is liberated. This is titrated with N/10 sodium thiosulfate.

One ml. of N/10 thiosulfate = 0.003269 gram H_2SO_4.[22]

DETERMINATION WITH STANDARD BARIUM CHLORIDE SOLUTION AND TETRAHYDROXYQUINONE INDICATOR[23]

Materials and Reagents.—Standard barium chloride solutions are prepared in any convenient range from 1 ml. equivalent to from 1–50 mg. of sulfate.

Indicator.—Disodium tetrahydroxyquinone, 1 part, ground with 300 parts of dried potassium chloride.

[18] Treadwell and Hall, "Analytical Chemistry," 2, 4th Ed., p. 716. Am. Jour. Sci. and Arts, **114**, 478.

[19] See p. 716, loc. cit.

[20] The barium chromate used should be free from soluble chromate, barium carbonate or soluble barium salt. The compound may be prepared by precipitating with potassium chromate added to a boiling solution of barium chloride. The precipitate is washed with boiling water containing a little acetic acid, and finally with pure water, and then dried. Four grams of the dry salt are dissolved in a liter of normal hydrochloric acid.

[21] In presence of iron, zinc and nickel, the solution is neutralized with ammonium hydroxide and an excess added; after boiling, the solution is filtered. By using calcium carbonate insoluble basic chromates of these elements would be formed, and low results for SO_3 would follow. This is avoided by the use of ammonia.

[22] $N/10\ Na_2S_2O_3 = \frac{H_2SO_4}{30} = 98.08 \div 30 = 3.269.$

[23] Schroeder, Ind. Eng. Chem., Anal. Ed. **5**, 403 (1933). This paper includes a bibliography of 120 references on the determination of sulfur. The application of the method to water analysis is described by Sheen and Kahler, ibid., **8**, 127 (1936); the same authors also applied the method to the determination of sulfur in rubber, ibid., **9**, 69 (1937). Details are quoted from the latter papers.

Procedure A.—Sulfate range up to 2000 parts per million. Twenty-five ml. of the solution is made just acid to phenolphthalein with 0.02 N hydrochloric acid. Twenty-five ml. of ethyl alcohol, isopropyl alcohol or alcohol denatured by formula No. 30 are added. The amount of indicator shown in the following table is added, and with the solution at 20 to 25° C. standard barium chloride solution is titrated in slowly with thorough agitation until the yellow color changes to rose.

Procedure B.—Sulfate range 2000 to 30,000 parts per million. Solid sodium chloride is to be added (see table). The neutralization and titration are as described under A.

Procedure C (with phosphate up to 60 parts per million).—Carefully neutralize a 25 ml. filtered sample with 0.02 N HCl until brom cresol green just changes to the acid tint (yellow range, pH about 4). Follow procedure A or B.

CONDITIONS FOR VARIOUS CONCENTRATIONS OF SULFATE

Sulfate Parts per Million	Amount of Indicator Mixture	$BaCl_2$ 1 ml. = mg. of SO_4	Sodium Chloride Needed, g.
Up to 100 *	0.1	1	—
100–1000 *	0.2	1	—
1000–2000	0.2	4	—
2000–4000	0.4	10	2.
4000–10000	0.4	10	4.
10000–20000	0.6	50	8.
20000–30000	0.8	50	8.

* Subtract 0.1 ml. as a blank correction.

Interference is caused by more than 5 parts per million of ferrous or ferric iron, by more than 6 p.p.m. of aluminum, or 60 p.p.m. of phosphate. Amounts of silicate up to 1500 p.p.m.; Mg up to 1440, Ca to 344 and Cl^- up to 15000 p.p.m. or higher do not interfere. In examining rubber, after oxidation by one of the standard methods, a measured excess of standard barium chloride is added, and the zinc, iron, etc. are precipitated by potassium hydroxide at pH 8.3 (barely alkaline to phenol phthalein), and the mixed precipitate is filtered off. The excess of barium in the filtrate is titrated with standard sodium sulfate, after the alkali has been neutralized with 0.02 N HCl. For percentages of sulfur ranging from 1.7 to 5.8 the maximum deviation from the percentage found gravimetrically was 0.05%.

BENZIDINE HYDROCHLORIDE METHOD—RASCHIG

Benzidine sulfate, $C_{12}H_8(NH_2)_2 \cdot H_2SO_4$, is scarcely soluble in water containing hydrochloric acid. The weak base benzidine is neutral to phenolphthalein and the acid in its sulfate may be titrated with an alkali.[24] The method gives reliable results in the analysis of all sulfates, provided no substances are

[24] Method suggested by Raschig, Z. anal. Chem., 42, 617 and 818 (1903).

present which attack benzidine, and provided the amount of other acids and salts present is not too great.[25]

Reaction.—$Na_2SO_4 + C_{12}H_8(NH_2)_2 \cdot 2HCl = 2NaCl + C_{12}H_8(NH_2)_2 \cdot H_2SO_4$ and

$$C_{12}H_8(NH_2)_2 \cdot H_2SO_4 + 2NaOH = C_{12}H_8(NH_2)_2 \cdot 2H_2O + Na_2SO_4.$$

Reagent.—***Benzidine hydrochloride*** is prepared by taking 6.7 grams of the free base, or the corresponding amount of the hydrochloride and mixing into a paste with 20 ml. of water in a mortar. Twenty ml. of hydrochloric acid (sp.gr. 1.12) are added and the mixture diluted to exactly 1000 ml. One ml. of this solution corresponds to 0.00357 gram H_2SO_4. The solution has a brown color. Brown flakes are likely to separate out on standing, but these do no harm.

Procedure.—The sulfate solution is diluted with water so that there is at least a 50-ml. volume for each 0.1 gram sulfuric acid present. An equal volume of the reagent is vigorously stirred in, and the precipitate allowed to settle for ten minutes. The solution is filtered onto a double filter, placed on a porcelain, perforated plate in a funnel (a Büchner is satisfactory), gentle suction being applied. The last portions of the precipitate are transferred to the filter by means of small portions of the clear-filtrate, and the compound then washed with 20 ml. of cold water added in small portions and sucked dry with each addition. The precipitate and filter are placed in an Erlenmeyer flask, 50 ml. of water added, and the mixture shaken until homogeneous. Phenolphthalein indicator is now added, the mixture heated to about 50° C. and titrated with N/10 sodium hydroxide. When the end-point is nearly reached, the liquid is boiled for five minutes, and the titration then completed.

$$\text{One ml. } N/10 = 0.004904 \text{ gram } H_2SO_4.$$

DETERMINATION OF FREE SULFURIC ACID

Other free acids being absent, sulfuric acid may be accurately determined by titration with standard alkali. The method for determining sulfuric acid in presence of commonly occurring acids, and in mixed acids are given in Volume II, in the chapter on Acids.

$$\text{One ml. } N/1\ NaOH = 0.04904 \text{ g. } H_2SO_4.$$

[25] Friedheim and Nydegger (Z. anal. Chem., 49, 464 (1910)) have found that there should not be more than 10 mol. HCl, 15 mol. HNO_3, 20 mol. $HC_2H_3O_2$, 5 mol. alkali salt, or 2 mol. ferric iron present to 1 mol. H_2SO_4. See Treadwell and Hall, "Analytical Chemistry," pp. 714–716.

DETERMINATION OF PERSULFATES

FERROUS SULFATE METHOD

Ferrous salts in cold solutions are oxidized to ferric form by persulfates. Advantage is taken of this action in the quantitative determination of persulfates.

Reaction.—$2FeSO_4 + H_2S_2O_8 = Fe_2(SO_4)_3 + H_2SO_4$.

Procedure.[26]—About 2.5 grams of the persulfate are dissolved in water and diluted to 100 ml. Ten ml. of this solution, equivalent to one-tenth of the sample, weighed out, are placed in a flask and a considerable excess of standard ferrous sulfate solution [27] added, say 100 ml. measured out from a burette. The solution is diluted with an equal volume of hot, distilled water (70 to 80° C.), and the excess ferrous sulfate titrated with N/10 potassium permanganate. This titration is deducted from the permanganate equivalent of 100 ml. of the ferrous solution taken (if this amount was used). The difference is due to persulfate oxidation.

One ml. N/10 $KMnO_4 = 0.009707$ gram $H_2S_2O_8$; or $= 0.01141$ gram $(NH_4)_2S_2O_8$; or $= 0.01352$ gram $K_2S_2O_8$.

OXALIC ACID METHOD

Oxalic acid, in presence of silver sulfate, reduces persulfates in accordance with reaction, $H_2C_2O_4 + H_2S_2O_8 = 2H_2SO_4 + 2CO_2$.

$$H_2C_2O_4 + H_2S_2O_8 = 2H_2SO_4 + 2CO_2.$$

Procedure.—About 0.5 gram of the persulfate is placed in an Erlenmeyer flask, 50 ml. of N/10 oxalic acid added, together with 0.2 gram silver sulfate in 20 ml. of 10% sulfuric acid solution. The mixture is heated on the water bath for about half an hour to expel carbon dioxide. When the evolution ceases the liquid is diluted to 100 ml. with warm water and titrated warm (about 40° C.) with N/10 potassium permanganate. The excess of oxalic acid is titrated, the difference is due to oxidation by the persulfate.

For calculation see factors in previous method.

ALKALI TITRATION OF THE BOILED SOLUTION

The aqueous solutions of potassium, sodium, and barium persulfates are decomposed by boiling as follows (M = metal Na, K, or Ba):

$$2M_2S_2O_8 + 2H_2O = 2M_2SO_4 + O_2 + 2H_2SO_4.$$

[26] Method suggested by Le Blanc and Eckardt, Chem. News, 81, 38 (1900).

[27] About 30 grams of ferrous sulfate or ferrous ammonium sulfate crystals are dissolved in 900 ml. of water and the volume made to 1000 ml. with concentrated sulfuric acid. The reagent is standardized against N/10 potassium permanganate and the value per ml. in terms of the standard permanganate noted, the ml. permanganate solution required divided by the ml. of ferrous sulfate solution taken for titration, gives value of the reagent in terms of the permanganate.

The solutions are best verified upon a persulfate of known purity.

Procedure.—About 0.2 g. of the persulfate salt is dissolved in 200 ml. of water and the solution boiled about 15 minutes, then cooled and titrated with N/10 NaOH, using methyl orange indicator.

One ml. N/10 NaOH = 0.02008 g. $BaS_2O_8 4H_2O$, or 0.01191 g. $Na_2S_2O_8$.

Ammonium persulfate cannot be determined by the above method but may be determined by the ferrous sulfate method—which see above.

DETERMINATION OF SULFUR IN COMBINATION AS SULFIDES, SULFITES, BISULFITES, METABISULFITES, THIOSULFATES, SULFATES AND HYDROSULFITES

AVAILABLE HYDROGEN SULFIDE IN MATERIALS HIGH IN SULFIDE SULFUR. IRON SULFIDE, SODIUM SULFIDE, ETC.

Evolution Method.—Since it is desired to obtain the H_2S that ordinarily would be obtained when the sulfide is treated with a strong acid, the mat of metallic aluminum or zinc and the addition of stannous chloride solution used in the procedure given on page 914 is omitted here.

Procedure.—0.5 to 1 gram of the sulfide is placed in the dry evolution flask. All connections are now made as directed in the general procedure. Three absorption bulbs containing neutral solution of cadmium sulfate are connected to the condenser, and supported by wires attached to the thistle tube and the arm of the condenser. All connections being tight, 100 ml. of dilute sulfuric acid, 1 : 4 are added through the thistle tube and H_2S evolved.

Titration.—When the evolution of the H_2S is complete, the bulbs containing the precipitate are emptied into a beaker and carefully washed out. The precipitate is now filtered and washed five or six times until free of acid. Methyl orange is added to the filtrate and the free acid titrated with N/10 NaOH.

The precipitate may be titrated with iodine according to (*b*) under general method of procedure, using an excess of iodine, followed by starch and acid and then titrating back with sodium thiosulfate solution. A double check may thus be obtained.

If it is desired to weigh the CdS precipitate, it is best to evolve the H_2S into a neutral solution of cadmium salt. The precipitate formed in a neutral or slightly acid solution is crystalline and easily filtered, whereas that formed in an ammoniacal solution is gelatinous.

When a neutral $CdSO_4$ or $CdCl_2$ solution is used, H_2S should be evolved by sulfuric acid and not by hydrochloric acid, as the latter is volatile, and will pass through the condensing bulb recommended in the general procedure.

One ml. N/10 NaOH = .001703 gram H_2S
" " = .004395 gram FeS
" " = .003903 gram Na_2S.

HYDROGEN SULFIDE AND SOLUBLE SULFIDES

Direct titration of hydrogen sulfide water, and soluble sulfides in solution may be made in absence of other substances acted upon by iodine. The solution containing the sulfide is added to an excess of N/10 iodine solution, made acid with hydrochloric acid, and the excess iodine titrated with N/10 sodium thiosulfate. The following reaction takes place:

$H_2S+I_2=2HI+S$. The ml. $Na_2S_2O_3$ are subtracted from ml. I = I reacting with H_2S. One ml. N/10 iodine = 0.001703 gram H_2S.

NOTE.—The soluble sulfide may be determined gravimetrically by oxidizing with bromine, the reagent being added until the solution is colored brownish red, the excess of the halogen removed by boiling and the sulfate precipitated as $BaSO_4$.

DETERMINATION OF A SULFIDE AND A SULFOHYDRATE IN PRESENCE OF EACH OTHER

When a mixture of sulfide and sulfohydrate is treated with iodine the following reactions take place:

$$H_2S+I_2=2HI+S \quad \text{and} \quad NaHS+2I_2=NaI+HI+S.$$

It will be noticed that the acidity produced by the first reaction is twice that caused by the iodine action on the sulfohydrate, and that the acidity in the latter titration remains unaffected. The reactions with the alkali salts is effected by addition of a standard iodine solution containing a known amount of hydrochloric acid. The reactions in this case are as follows:

$Na_2S+2HCl=2NaCl+H_2S$ and $NaSH+HCl=NaCl+H_2S$. The iodine reacts with the H_2S as follows: $H_2S+I_2=2HI+S$.

From the second set of reactions it is evident that the quantity of hydriodic acid formed by the action of iodine on the sulfide is equivalent to the hydrochloric acid required to decompose the sulfide, so that the acidity remains unchanged. On the other hand with sulfohydrate, NaSH, the hydriodic acid formed by the iodine oxidation, is twice the equivalent of hydrochloric acid required to decompose the acid salt. Hence it is evident that the acidity is a measure of the quantity of sulfohydrate present in the mixture. From the second set of reactions the following procedure is devised.

Procedure.—To a measured amount of N/10 iodine solution containing a measured amount of N/10 hydrochloric acid (the mixture diluted to 400 ml.) is added the solution containing the sulfide and sulfohydrate from a burette, until the stirred solution becomes a pale yellow color. (The ml. of solution added is noted and its equivalent of the sample calculated.) Starch is now added and the excess of the iodine titrated with N/10 sodium thiosulfate. The ml. of thiosulfate in terms of N/10 solution subtracted from the ml. N/10 iodine solution taken give ml. iodine required by the sample added. The acidity of the solution is now determined by titration with N/10 sodium hydroxide. The ml. NaOH required by the HI give total NaOH minus ml. N/10 HCl present in the iodine solution.

Calculation.—*A*. Ml. N/10 iodine required by the sample minus twice the ml. of N/10 NaOH required by HI formed by the reaction multiplied by 0.003903 give weight of Na_2S, (i.e., ml. I–2 ml. NaOH)$\times$0.003903 = gram Na_2S.

B. Ml. N/10 NaOH required by the HI multiplied by 0.005607 gives gram weight of NaHS. Or in brief: ml. NaOH$\times$0.005607 = gram NaHS.

The above weights multiplied by 100 and divided by the weight of sample used in the iodine titration give per cent of constituents in the sample.

The method is of value in the analysis of alkali sulfides in absence of other compounds, which are decomposed by hydrochloric acid and which react with iodine.

DETERMINATION OF THIOSULFATE IN PRESENCE OF SULFIDE AND SULFOHYDRATE

The sulfide and sulfohydrate sulfur is removed from the solution by adding an excess of freshly precipitated cadmium carbonate. The solution is filtered and diluted to a definite volume and the thiosulfate determined on an aliquot portion by running it into an excess of N/10 iodine solution and titration the excess of iodine with N/10 thiosulfate solution.

$$\text{One ml. N/10 iodine} = 0.02482 \text{ gram } Na_2S_2O_3 \cdot 5H_2O.$$

DETERMINATION OF SULFATES AND SULFIDES IN PRESENCE OF ONE ANOTHER

In one portion of the sample the sulfide is decomposed and the hydrogen sulfide expelled by boiling the solution (in presence of CO_2 replacing air in the flask) after acidifying with hydrochloric acid. The sulfate sulfur may now be precipitated as $BaSO_4$ by the usual methods.

In a second portion total sulfur is determined after oxidizing the sulfide with an excess of bromine and boiling out the excess of halogen. Total sulfur minus sulfate sulfur = sulfide sulfur.

The sulfide may be oxidized with fuming nitric acid by boiling the solution in a flask with reflex condenser. The nitric acid is expelled by evaporating the solution down to a moist residue. The sulfate is now precipitated by taking up the residue with water, adding HCl and then sufficient $BaCl_2$ to cause complete precipitation.

DETERMINING THE SULFUR IN THIOCYANIC (SULFOCYANIC) ACID AND ITS SALTS

Oxidation of the sulfur may be accomplished as described for sulfides in the preceding method either by means of bromine or by fuming nitric acid. The sulfur is then precipitated as $BaSO_4$ as usual.

DETERMINATION OF SULFUROUS ACID (SO_2 IN SOLUTION) FREE, OR COMBINED IN SULFITES, ACID SULFITES, META-BISULFITES AND THIOSULFATES

Gravimetric Method, Oxidation to Sulfate and Precipitation as $BaSO_4$.—Sulfur dioxide, free or combined in a soluble salt, may be oxidized to SO_3 or sulfate by means of an oxidizing agent such as chlorine, or bromine, or hydrogen peroxide (alkaline solution). The sulfuric acid or sulfate may be then precipitated and determined as $BaSO_4$ in the usual way.

Procedure.—The halogen (bromine preferred) is added (in a water-saturated solution) in large excess to the sample, the free halogen then boiled out, and

sulfuric acid precipitated, from a solution made slightly acid with hydrochloric acid, by addition of a solution of barium chloride, according to the standard procedure.

If hydrogen peroxide is used, the solution should be made alkaline with ammonia and the peroxide added, the excess boiled out, and the solution then made acid as directed above.

$BaSO_4 \times 0.356 = H_2SO_3$, or $\times 0.5400 = Na_2SO_3$, or $\times 0.4458 = NaHSO_3$, or $\times 0.3387 = Na_2S_2O_5$, or $\times 0.2744 = SO_2$.

NOTE.—If hydrogen peroxide is used, it should be tested for H_2SO_4 and allowance made accordingly.

VOLUMETRIC METHODS

Titration with Iodine. Sulfurous Acid, Sulfites, Metabisulfites, Thiosulfates.—Sulfurous acid, combined or free, may be titrated with iodine solution, the following reaction taking place:

$$SO_2+2I+2H_2O=H_2SO_4+2HI.$$

The titration is accomplished by adding the solution of sulfurous acid, sulfite, or thiosulfate to the iodine, not in the reverse order, since in the latter order low results are obtained, unless the solution is very dilute (less than 0.04% SO_2).[28]

Procedure.—Five grams of the sample (sulfurous acid solution titrated directly) are dissolved in a little water and transferred to a 500-ml. graduated flask, then made to volume. Each ml. of this solution contains 0.01 gram of the sample; 100 ml. of N/10 iodine, or their equivalent if the solution is stronger or weaker, are placed in a beaker together with a few drops of hydrochloric acid. A portion of the sample in a 100-ml. burette is now run into the iodine, with constant stirring, until the color of the free iodine has almost faded out; a little starch solution is now added and the titration continued to the complete fading of the blue color.

Since each ml. of the sample contains 0.01 gram of the material, it follows that the 100-ml. iodine equivalent in terms of the material titrated expressed to the fourth decimal place as a whole number, if divided by the ml. of the sample required, will give the per cent of the substance sought, provided other titratable substances are absent.

Example.—Suppose *sodium sulfite* is being titrated, then since 100 ml. of N/10 iodine are equivalent to 0.6303 gram Na_2SO_3, 6303 divided by the ml. Na_2SO_3 solution required gives per cent Na_2SO_3. If 63 ml. were required the salt would be 100% pure.

NOTE.—When the iodine equivalent is over unity, it is necessary to take a larger sample per 500-ml. volume to avoid having a titration of over 100 ml. For example in the *analysis of sodium thiosulfate*, a 20-gram sample is diluted to 500 ml. and a portion of this added to 100 ml. of N/10 iodine solution. In this case it must be kept in mind that each ml. of the sample contains 0.04 gram of thiosulfate and the percentage calculated accordingly upon completing the titration.

[28] A secondary reaction takes place, the hydriodic acid formed reducing the SO_2 to S, e.g., $SO_2+4HI=2H_2O+2I_2+S$. (J. Volhard, Ann. d. Chem. u. Pharm., 242, 94.) The solution, if not too dilute, will show a distinct separation of sulfur. (Treadwell and Hall, "Analytical Chemistry," 2, 3d Ed.) Raschig believes that a loss of SO_2 occurs, due to evaporation. (Z. Angew. Chem., 580 (1904).) See Sutton, "Volumetric Analysis," 10th Ed., pp. 128, 129. Gooch, "Methods in Chemical Analysis," 1st Ed., pp. 364–368.

If the titration of the iodine is made in a casserole, the end-point may readily be recognized without the addition of starch.

Equvalents.—One hundred ml. N/10 iodine solution will oxidize:
Sodium sulfite (anhydrous), $Na_2SO_3 = 0.6303$ gram, or 0.3203 gram SO_2.
Sodium sulfite, $Na_2SO_3 \cdot 7H_2O = 1.2608$ grams.
Acid sodium sulfite, $NaHSO_3 = 0.5203$ gram.
Sodium metabisulfite, $Na_2S_2O_5$ (anhydride of $NaHSO_3$) $= 0.4753$ gram.
Sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O = 2.4819$ grams.

NOTE.—Hydrogen sulfide or sodium sulfide are also titrated with iodine. Equivalents for 100 ml. N/10 iodine $= 0.1703$ gram H_2S, or 0.3903 gram Na_2S.

Determination of Sodium Thiosulfate.—The iodine titration is described on page 926. See also the chapter on Iodine.

ACIDIMETRIC AND ALKALIMETRIC METHODS

Titration of Sulfites, Acid Sulfites (Metabisulfite) or Sulfurous Acid.—The choice of indicator is important as the titration with one may be different from that obtained in presence of another. For example the titration of sulfurous acid by an alkali in presence of phenolphthalein is twice the titration necessary to obtain an alkaline reaction with methyl orange. The reason for this is evident by the fact that Na_2SO_3 is neutral to phenolphthalein and alkaline to methyl orange, whereas $NaHSO_3$ is neutral to methyl orange but is acid to phenolphthalein. Advantage is taken of this in the analysis of salts containing a mixture of the normal and acid salts.

Reaction.—With phenolphthalein $H_2SO_3 + 2NaOH = Na_2SO_3 + 2H_2O$.
With methyl orange $H_2SO_3 + NaOH = NaHSO_3 + H_2O$.

On the other hand if a salt is being titrated, methyl orange cannot be used for the titration of metabisulfite or acid sulfite, since these salts are neutral to this indicator, here phenolphthalein is required and an alkali titration made.

Reaction.—$NaHSO_3 + NaOH = Na_2SO_3$. ($Na_2S_2O_5 + H_2O = 2NaHSO_3$.)

Again if sodium sulfite, Na_2SO_3, is to be titrated, phenolphthalein would not do as an indicator, since Na_2SO_3 is neutral to this indicator. Here an acid titration is required with methyl orange indicator present:

$$2Na_2SO_3 + H_2SO_4 = 2NaHSO_3 + Na_2SO_4.$$

A. Sulfurous Acid

For the alkali titration of this acid it is advisable to use methyl orange as indicator, since this is not affected by carbon dioxide, which is very frequently present.

Reaction.—*$H_2SO_3 + NaOH = NaHSO_3$.*
One ml. N/1 NaOH $= 0.06406$ gram SO_2, or $= 0.08208$ gram H_2SO_3.

B. Sodium Metabisulfite

Sodium acid sulfite does not exist in dry form, since the salt loses water and anhydrous $Na_2S_2O_5$ results. This is analogous to sulfurous acid, which exists only in water solution. It has been found that the acid sulfite solution evaporated to crystallization yields a product, which though dried with extreme

care, forms the anhydrous salt, $Na_2S_2O_5$. For correct report, therefore, the solid should be reported as metabisulfite, and the solution of the salt as acid sulfite.

Since metabisulfite in solution, or acid sulfite, is neutral to methyl orange, phenolphthalein indicator must be used and an alkali titration made. Carbon dioxide-free water and reagents should be used.

Reaction.—

$$Na_2S_2O_5+H_2O=2NaHSO_3 \text{ and } NaHSO_3+NaOH=Na_2SO_3+H_2O.$$

Procedure.—9.506 grams of the finely ground powder are dissolved in about 50 ml. of cold saturated salt solution, to which has been added from a burette 50 ml. of normal sodium hydroxide. The salt solution should be made neutral to phenolphthalein. One ml. of 0.1% solution of the indicator is added and the excess acid sodium sulfite titrated with normal sodium hydroxide until a permanent faint pink color is obtained.

Since the normal equivalent of the salt has been taken for analysis the ml. alkali titration, including the 50 ml. originally present, will give the percentage directly in terms of $Na_2S_2O_5$.

NOTE.—The NaCl serves to give a sharp and more permanent end-point. It may be necessary to add more of the indicator towards the end of the titration.

C. SODIUM SULFITE, Na_2SO_3

Sodium sulfite, Na_2SO_3, is neutral to phenolphthalein and alkaline to methyl orange. The titration of this salt is accomplished by addition of standard acid in presence of methyl orange.

Reaction.—$2Na_2SO_3+H_2SO_4=Na_2SO_4+2NaHSO_3$.

Procedure.—The normal factor weight (12.6 grams) of the salt is dissolved in about 250 ml. of distilled water, 1 ml. of methyl orange added, followed by normal sulfuric acid, added from a burette until a faint orange end-point is obtained. As in the case of the metabisulfite, each ml. of normal sulfuric acid equals 1% Na_2SO_3. Hence the percentage is obtained directly from the burette reading.

NOTES.—Organic coloring matter may be removed from the solution by filtering through charcoal.

If sodium carbonate is present, it will also be titrated. A correction must be applied for this. In the presence of sodium carbonate the solution will be alkaline to phenolphthalein. An approximate estimation of this may be obtained by titration with normal acid in presence of this indicator, remembering that sodium bicarbonate, $NaHCO_3$, is neutral to phenolphthalein, hence twice this titration must be deducted from the total methyl orange titration, i.e., $Na_2CO_3+H_2SO_4$ (M.O.) $=Na_2SO_4+H_2CO_3$ and $2Na_2CO_3+H_2SO_4$ (P.) $=2NaHSO_4+2NaHCO_3$. (Alkaline hydroxides will also be titrated.) CO_2 may also be obtained by the standard procedure under carbon, the SO_2 being oxidized by addition of chromic acid. $Na_2CO_3\times1.8=$ equivalent Na_2SO_3.

Sodium carbonate may be detected in a sulfite or metabisulfite by adding cold, dilute acetic acid (25%) to the dry powdered salt. An effervescence is due to the presence of carbonate, since a sulfite or metabisulfite does not effervesce under similar conditions.

DETERMINATION OF SULFITES, METABISULFITES, THIOSULFATES, SULFATES, CHLORIDES AND CARBONATES IN PRESENCE OF ONE ANOTHER

1. Sodium Sulfite, Na_2SO_3

This is determined by titration with standard acid in the presence of methyl orange indicator according to the standard procedure previously described. If a carbonate is present, allowance must be made for this as stated

One ml. N/1 $H_2SO_4 = 0.1261$ gram Na_2SO_3. *Calculate to per cent.*

$Na_2CO_3 \times 1.8 =$ equivalent Na_2SO_3.

2. Sodium Metabisulfite, $Na_2S_2O_5$

This is determined by titration with a standard alkali in the presence of phenolphthalein indicator according to the procedure previously described.

One ml. N/1 $NaOH = 0.09506$ gram $Na_2S_2O_5$. *Calculate to per cent.*

3. Sodium Thiosulfate, $Na_2S_2O_3$

One gram of the mixed salts is placed in 100 ml. of N/10 iodine solution, and the excess of iodine titrated with N/10 sodium thiosulfate according to the standard procedure.

Calculation.—$\{(\text{ml. N/10 I} - \text{ml. N/10 } Na_2S_2O_3) - [(\% \; Na_2S_2O_5 \times 2.104) + (\% \; Na_2SO_3 \times 1.5865)]\} \times 1.5811 = \% Na_2S_2O_3$.

4. Sodium Sulfate

The sample is dissolved in a little water, hydrochloric acid added, and the solution boiled to expel all of the SO_2. Barium sulfate is now precipitated and determined according to the standard procedure.

$BaSO_4 \times 0.6086 = Na_2SO_4$.

Note.—The amount of the sample required is governed by the per cent Na_2SO_4 present.

5. Sodium Chloride

The sample is dissolved in water, nitric acid added and the solution boiled until all the SO_2 has either been volatilized or oxidized. The chlorine of the chloride is now precipitated with silver nitrate from a hot solution by the usual procedure.

$AgCl \times 0.4078 = NaCl$.

Note.—The amount of the sample taken is governed by the per cent of NaCl present.

6. Sodium Carbonate, Na_2CO_3

Carbon dioxide is evolved from the mixture by means of chromic and sulfuric acids, the former being used to oxidize the SO_2 of the sample. The evolved gas is bubbled through a mixture of concentrated sulfuric and chromic acids to remove any SO_2 that may have escaped oxidation, Fig. 34. The CO_2 is absorbed either in caustic and weighed or is passed into a standard solution of barium hydroxide and titrated according to the standard procedures given under carbon.

Note.—The amount of the sample taken is governed by the per cent of Na_2CO_3 present.

ESTIMATION OF SODIUM HYDROSULFITE

Standard Indigo Solution.—To about 150 ml. concentrated sulfuric acid in a casserole, are added 4.2 grams of indigo, slowly with stirring. The solution is kept at 80° C. for an hour in an oven, stirring once or twice during this time. After cooling the solution it is made up to four liters with distilled water. This reagent is now standardized against N/50 $KMnO_4$ solution. To do this 25 ml. of the indigo solution is diluted in a casserole with 300 ml. of water and titrated with N/50 $KMnO_4$ reagent.

One ml. N/50 $KMnO_4$ is equivalent to 0.0015 g. indigotin.

$1.505:1 =$ gram indigotine : x, where $x =$ gram $Na_2S_2O_4$ in 25 ml. Indigo solution. $\frac{2 \times 10{,}000}{\text{ml. titration}} = Na_2S_2O_4$ (2.5 grams of solid) or grams per liter (25 ml. sample made up to 500 ml.).

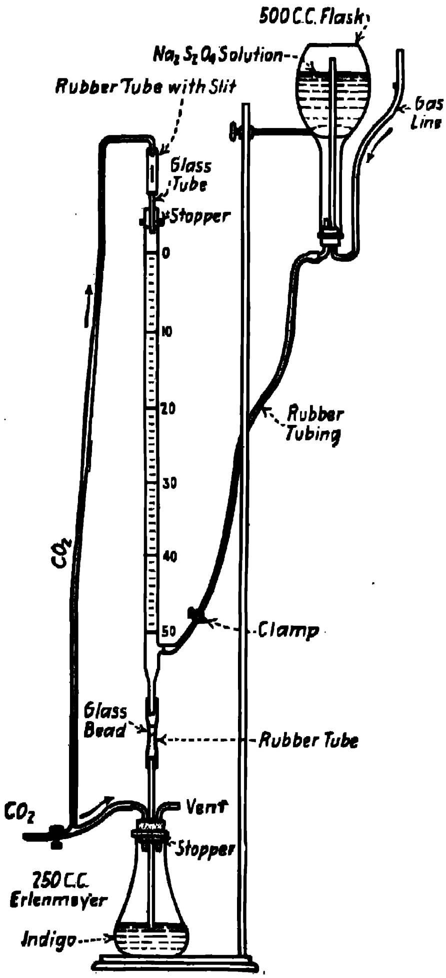


FIG. 114. Apparatus for Determining Hydrosulfite.

Procedure.—Titration of Sodium Hydrosulfite Against Standard Indigo Solution.—Fifty ml. of standard indigo solution are pipetted into a 300 ml. Erlenmeyer flask. The titrating apparatus as well as the 500 ml. volumetric flask are filled with CO_2 gas (C_2H_2 may be used in place of CO_2). Two and a half grams of the solid are now taken, or 25 ml. of the solution (if the material is already dissolved as a 10% solution) and placed in the 500 ml. flask and made to mark with distilled water. The flask is stoppered and connections made with the burette, etc., as shown in Fig. 114. The burette is filled with the sample and the flask containing the indigo solution is placed under the burette as shown in the figure. The air is displaced from the apparatus by CO_2, the flow of this gas being continued during the titration. The hydrosulfite solution is now added to the indigo solution until it changes from the blue to a yellow or brown color.

$$\frac{\text{Factor for Indigo}}{\text{ml. titration}} = \%\ Na_2S_2O_4 \text{ in solids, or grams per liter in liquids.}$$

NOTES.—The hydrosulfite solution should be made alkaline with NaOH, then made up rapidly to volume and titrated in an atmosphere of CO_2 to prevent oxidation.

The size of the sample may be varied, but the titration should be over 10 ml.

The tip of the burette should dip below the surface of the indigo until near the end-point, then withdrawn and the titration completed with the tip above the surface.

The above method was outlined by J. H. Brackett.

DETERMINATION OF FREE SULFUR IN A MIXTURE

Free sulfur is an essential constituent in many types of mixtures and the method of estimation will vary with the nature of the other ingredients. Hydrated lime, chalk, gypsum, dry lime sulfur, calcium arsenate, nicotine sulfate in infusorial earth carrier, sodium polysulfide, sodium chloride, epsom salts, and the usual fertilizer materials are the substances most commonly found in the mixtures now on the market. All commercial forms of sulfur are found in these mixtures and the value of the mixture usually depends largely on which form of sulfur was used. For example, an insecticide dust containing coarse crude or refined sulfur, instead of flowers or superfine, would be valueless even though the chemical analysis showed that the mixture contained the specified percentage of total sulfur. Therefore, the microscope and a little ingenuity will indicate the proper combination of methods to follow.

From 1 to 10 grams of the material, depending upon the amount of sulfur present, is extracted in a Soxhlet extractor (see modified form, Fig. 115) with carbon bisulfide (freshly distilled) for twelve hours. The extract is evaporated to dryness, adding 10 ml. of bromine-carbon tetrachloride mixture together with 15 ml. of nitric acid. The residue is taken up with 10 ml. of hydrochloric acid, diluted with 150 ml. of distilled water, heated to boiling and the sulfuric acid precipitated with 10% barium chloride solution, washed, dried, ignited and weighed according to the procedure for sulfur.

$$\frac{BaSO_4 \times 100 \times 0.1373}{\text{Weight of sample}} = \%\ \text{free rhombic sulfur.}$$

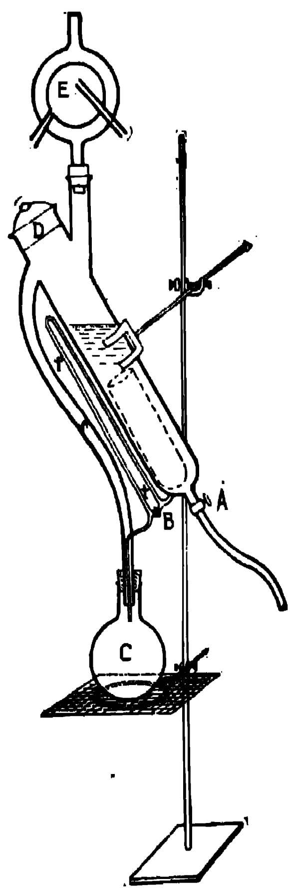


FIG. 115. Sanders' Extraction Apparatus.

After extraction carefully dry the thimble and contents. Examine under a microscope a small portion of the dried material. Remaining sulfur if present will be in the amorphous form and have the characteristic "droplet" structure seen in

flowers of sulfur. Presence of much sulfur at this stage indicates that flowers of sulfur were used in the mixture, and the proper procedure to follow will depend on the nature of the other constituents. If a soluble sulfate such as nicotine sulfate or epsom salts is indicated, then an aliquot of the residue in the extraction thimble can be leached with hot water and the sulfur determined by one of the usual methods after wet oxidization. If an insoluble material such as gypsum is indicated, then the free sulfur may be burned off in the air and the combined sulfur determined in the residue after solution by one of the standard methods; the total sulfur having first been determined in another aliquot after wet oxidation with bromine and nitric acid. Whatever procedure is followed, the content of amorphous sulfur is calculated by difference and thus the percentage of flowers established by adding the amount thus found to the CS_2 soluble sulfur.

Sanders' extraction apparatus [29] has several advantages that make this apparatus desirable for laboratory use, where a number of daily extractions are required. As may be seen from Fig. 115, by simply removing the glass stopper *D* the cylinder may be charged without disconnecting the apparatus, as is necessary with the Soxhlet type of apparatus. The extraction is carried on with the traps *A* and *B* closed, the siphon *t–t'* acting automatically as in case of the Soxhlet. With *A* closed and *B* open the apparatus may be used as a reflux condenser. The solvent liquid may be drawn off by opening *A*. With *B* closed and *A* open the apparatus may be used as a condenser and the ether, chloroform, carbon disulfide, etc., distilled from *C*. The globe-shaped Soxhlet condenser may be replaced by Allihn's or Liebig's condenser, if desired. The ball form, however, is more compact.

EVALUATION OF SPENT OXIDE FOR AVAILABLE SULFUR

Spent oxide is the by-product of gas works, and refers to the spent Fe_2O_3 used in the scrubber for the removal of hydrogen sulfide from the gas. The FeS, as in case of pyrites, is used in the manufacture of sulfuric acid, and is evaluated by its available sulfur content.

Total Sulfur.—The oxide is sampled, brought into solution and the sulfur determined exactly as is given under the standard method for determination of sulfur in pyrites ore.

Residual Sulfur.—Two grams of the material are ignited to expel volatile sulfur, a porcelain crucible being used. The residue is treated with concentrated hydrochloric acid and after digestion on the steam or water bath is diluted with water and filtered. (If SiO_2 is present evaporation to dryness is necessary.) Sulfur is determined in the filtrate as usual.

[29] J. McC. Sanders, Proc. Chem. Soc., 26, 227–228 (1910). The Analyst, 35, 556 (1910).

Available Sulfur.—The per cent of residual sulfur is subtracted from the per cent total sulfur, the difference being available sulfur.

Iron.—This may be determined on an ignited sample according to a standard procedure for iron. See chapter on Iron.

ANALYSIS OF REFINED SULFURS AND BRIMSTONE

The impurities in commercial sulfurs and brimstones are seldom more than a few tenths per cent. Arsenic, acidity, chlorine, and the amount of amorphous sulfur present (CS_2 insoluble) are required. Also the fineness and specific volume (degrees Chancel) are often required for sulfurs used in agriculture.

Moisture.—The powdered sample, weighing 50 grams, is spread out on a watch-glass and dried for an hour at 100° C., then cooled in a desiccator and weighed.

Loss of weight in grams multiplied by 2 = per cent moisture.

Arsenic.—Ten grams of the material are treated with 30 ml. of carbon tetrachloride mixture (3 parts CCl_4 + 2 parts Br) and after standing for ten minutes 25 ml. concentrated nitric acid are added in small portions (a watch-glass covering the beaker during the intervals of addition). HNO_3 and Br are expelled by evaporation on the steam bath. Water is added and the evaporation repeated. Arsenic is now determined on the residue by the Gutzeit Method for arsenic.

NOTE.—Arsenic-free reagents should be employed.

Chlorine.—One hundred grams of the brimstone are extracted with hot water, the filtered extracts oxidized with 10 to 15 ml. of nitric acid and a few crystals of ammonium persulfate by boiling and treated with 5 ml. of 10% solution of silver nitrate. The solution, brought to boiling, is placed in a dark place and the silver chloride allowed to settle. This is now filtered off in a weighed Gooch crucible and chlorine calculated from the AgCl.

$$AgCl \times 0.2474 = Cl \text{ or } = 0.4078 = NaCl.$$

Mineral and Organic Impurity.—Ash 100 gms. of the sample by igniting a little at a time in a tared porcelain or silica ware dish. Carry on the combustion in plenty of air and *without* the aid of any external heat except toward the last. In igniting the sample use a small pin flame gas jet such as the petroleum chemist uses in making flash and fire tests. Do not use match or taper or alcohol to ignite the sulfur as a small amount of organic matter is certain to get into the sample from these sources and cause trouble in the combustion. The sulfur once ignited will burn evenly and clean unless organic matter is present. All refined sulfurs should burn completely without the aid of any external heat.

With American Gulf Coast brimstone and with oil or asphalt contaminated sulfur the organic matter present in even minute amount will cause trouble in burning unless special precautions are taken. A film of melted asphalt or oily matter forms over the surface of the molten sulfur and shuts off the air so that the flame from the burning sulfur is put out. When this film of dark oily matter is first noticed, touch it lightly with the pin flame and it will usually break or char, allowing the sulfur to burn evenly. Toward the last apply very gentle heat to the dish and thus char the organic matter but keep the temperature well below the red so that this organic material is not ignited. When all the sulfur is burnt off as indicated by no more odor of SO_2, cool the dish and weigh; this weight giving the combined organic and mineral matter. Then ignite the residue at low red heat to burn off all organic material; again cool and weigh; this weight giving the mineral impurity or ash. The difference between the two weights represents the organic impurity.

Acidity.—Boil 100 gms. of the pulverized sample with about 500 ml. water. The addition of a little neutral alcohol at the start will aid in wetting the sulfur which sometimes floats and causes trouble. Cool and make up to a standard volume. Pipette or filter off an aliquot and titrate with N/10 alkali, using phenolphthalein. Calculate acidity as H_2SO_4 and express as per cent acidity.

Available Sulfur.—Add together moisture, organic matter, ash, arsenic, acidity, chlorine and report available sulfur as the difference.

Amorphous Sulfur (CS_2 insoluble).—Weigh five to twenty grams of the finely pulverized sample into a tared extraction thimble and extract with carbon bisulfide. The rate of extraction is regulated so that one filling of the chamber takes about five minutes. The extraction should be complete in thirty minutes. It is important that the extraction be stopped as soon as the loss in weight of the thimble and contents becomes constant as long-continued extraction will carry some of the amorphous sulfur into solution. Note: A Soxhlet type extraction apparatus is best as other types where the thimble is not immersed in the liquid give erratic results at times on account of the tendency of the CS_2 solution of sulfur to " crawl " to the top of the thimble and there deposit out a hard scale of rhombic sulfur. When the extraction is completed, the thimble and contents are freed from CS_2 by exposure to a rapid current of dry air and then dried for thirty minutes in a water oven through which air circulates. (Finely divided sulfur, CS_2, and air is a mixture liable to spontaneous combustion, so get rid of the bulk of the CS_2 in the cold dry air current before exposing to the heat of the oven.) The weight of the contents of the thimble less ash and arsenic and organic matter is taken as the amorphous sulfur. Flowers of sulfur must contain in excess of 30% amorphous sulfur. (Flowers are often sophisticated by the addition of ground sulfur when the content of amorphous sulfur is lowered in proportion—this should not be reported as flowers but flowers with so much adulteration.) Refined lump sulfur, roll sulfur and rubber maker's sulfur should contain no amorphous sulfur. Powdered sublimed sulfur usually contains some small percentage of amorphous sulfur. Note: Direct sunlight, heat and some chemical fumes cause the amorphous sulfur in flowers to revert to the soluble rhombic modification. Therefore be careful in the preparation and treatment of samples of flowers of sulfur.

Fineness and Specific Volume of Degree Chancel.—Examine the sample under the microscope. Use a recessed slide and wet the specimen with alcohol

or preferably with concentrated sulfuric acid. Flowers of sulfur appear as loose agglomerations of opaque yellow spherical droplets. Ground refined sulfur and ground brimstone appear as clear angular fragments almost colorless. High quality flowers consist entirely of minute droplets all of uniform size and barely touching each other. In low quality flowers the droplets are of large and irregular size and are more or less fused together. The smaller and the more uniform the size of the sulfur particles—whether the droplets of the flowers or the grains of a pulverized sulfur—the greater will be the specific volume and and the degree Chancel. This is determined by the Chancel Sulfurimeter,[80] a tall glass tube, glass-stoppered, graduated into 100 degrees of ¼ ml. each. Five grams of the sulfur sample are accurately weighed out and dusted into the tube which is half filled with ether or alcohol. The sulfur and alcohol is strongly shaken and the tube and contents allowed to stand in a vertical position. The reading of the sulfur level is taken as soon as the subsidence ceases or at the end of an hour and this is reported as the degree Chancel. (If a Chancel Sulfurimeter is not obtainable, a tall glass-stoppered graduate of 25 ml. capacity will serve, remembering that each quarter ml. represents a degree in the Chancel scale. Of course this reading will not be as accurate as on the Sulfurimeter where the scale is larger on account of the smaller diameter of the Chancel tube.)

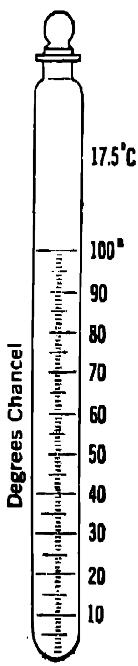


FIG. 116. Sulfurimeter.

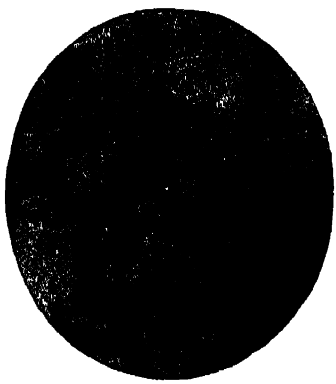


FIG. 117. Flowers of Sulfur.

FIG. 118. Rhombic Sulfur.

The cylindrical glass tube should have the following dimensions: The cylinder should be 23 cm. long and 15 mm. in diameter, with a scale starting from below, graduated upwards into 100 degrees, each degree being ¼ ml.; the 100 degrees (25 ml.) occupy a length of 100 mm. The cylinder is closed at the lower end, and glass stoppered, as shown in Fig. 116. The sulfur is first passed through a sieve 1 mm. mesh, in order to break down the lumps formed with storage. As stated, a 5 gram sample is placed in the tube and this half filled with anhydrous ether, having a temperature of 17.5° C. The sieved sample is

[80] Lunge, Tech. Methods of Chem. Anal., Vol. I, p. 265 (1908); Lunge, Sulfuric Acid and Alkali, Vol. I, Part 1, page 47 (1913).

shaken and additional ether added until the level stands 1 ml. over the 100° mark and the whole again shaken in an upright position, the sulfur allowed to settle and the degrees Chancel read off.

The procedure for analysis of refined sulfurs was contributed by Chas. A. Newhall.

QUANTITATIVE ESTIMATION OF SMALL QUANTITIES OF SULFIDE SULFUR; METHOD OF W. A. DRUSHEL AND C. M. ELSTON [31]

The method is a colorimetric method and consists essentially of the comparison of the depth of color of lead sulfide stains obtained from the sulfide sulfur of a given weight of a sample to be analyzed with a standard series of stains prepared from sulfide solutions of known sulfur content. A set of stains varying in depth of color from a faint yellowish brown to black representing from 0.0002% to 0.004% of sulfide sulfur may be prepared and used indefinitely for comparison. With a set of standard stains at hand the method has the advantage that within the range given the sulfide sulfur of a sample may be determined with a fair degree of accuracy in less than ten minutes.

Preparation of Standard Set of Sulfide Stains.—The apparatus used for preparing standard stains and for making analyses is very simple. The inner tube of a Liebig condenser with its larger end about 18 mm. in internal diameter is cut off 15 cm. in length. The smaller end is drawn down somewhat, rounded and fitted to a sound cork stopper which in turn is fitted to a 100 ml. round-bottom flask. The condenser tube then serves as a sort of reflux condenser. To the upper and larger end of this tube a filter paper moistened with a dilute solution of lead acetate is smoothly fitted and tied, so that the steam passing up through the tube and carrying hydrogen sulfide is required to pass out through the lead acetate paper. A similar tube with the internal diameter of its larger end about 36 mm. is also prepared and used for sulfide sulfur samples containing 0.001% or more of sulfur.

A solution of sodium sulfide is made up with pure distilled water and carefully standardized. The solution is then diluted to contain exactly 0.01% of sulfide sulfur. This solution is used for making up standard solutions containing 0.0002, 0.0004, 0.0006, 0.0008, 0.001, 0.002, 0.003 and 0.004% of sulfide sulfur respectively, taking care to use distilled water free from traces of nitrites in making the dilutions. It is found that the more dilute sulfide solutions when made up with ordinary distilled water lose their sulfide content either wholly or in part on standing for several hours in stoppered bottles. This difficulty is obviated by using nitrite free distilled water in making up the solutions.

Carefully measured portions of .1 ml. to 5 ml. of the standard solutions are pipetted into the 100 ml. flask and 25 ml. of hydrochloric acid of about 0.5% strength is added. The flask is immediately attached to the condenser tube

[31] Am. J. Sci., Fourth Series, 42, No. 248 (1916).

fitted with moistened lead acetate paper as previously described. The mixture is then gently boiled for a few minutes at such a rate that the steam issued not too rapidly from the upper end of the condenser tube. In this way the sulfide sulfur is quantitatively liberated as hydrogen sulfide and evenly deposited as lead sulfide on the moistened lead acetate paper. The undecomposed lead acetate is then washed out, the paper dried and labeled with the amount of sulfide sulfur present as one of the set of standard stains. In the same way complete sets in duplicate are prepared ranging in sulfide sulfur from 0.0002% to 0.004%.

DETERMINATION OF SULFUR IN CRUDE SULFUR BY CARBON BISULFIDE EXTRACTION METHOD [32]

Apparatus.—Two ground glass stoppered weighing bottles (diameter 30 mm., height 60 mm.), Munktell's No. 00, 9 cm. filter paper.

Procedure.—This determination is always run in duplicate.

A sheet of the filter paper is carefully and gently rubbed on both sides with a cloth to remove any free or loose fuzz from its surface. The paper is then folded and placed in a funnel where it is washed three or four times with C.P. carbon bisulfide. After draining, the paper is removed from the funnel by one side and slipped into the glass weighing bottle. The cover is fitted loosely in the bottle, and the bottle is dried at 40° to 50° C. for one hour; the drying is continued at 100° C. to constant weight. This second period of drying should require a minimum of one hour. The weighing bottle on being removed from the oven is tightly covered, cooled in a desiccator to room temperature, and carefully weighed. Previous to weighing, the tightly stoppered bottle should be momentarily opened to allow the air pressure inside the bottle to reach that of the atmosphere.

The paper is then removed from the tube and placed in a funnel. Three grams of the finely ground dried sulfur [33] is weighed out on a counter-poised watch glass, and brushed into the filter paper. The paper and its contents are then extracted several times with C.P. carbon bisulfide until the filtrate shows no traces of sulfur, and no sulfur is on the filter paper or around its edges.[34] The paper and the residue from the sulfur is transferred back to the

[32] Standard Methods of the Freeport Sulfur Co., through the courtesy of J. B. Chatelain.

[33] The dried sample from the moisture determination is usually and preferably used.

[34] In the case of refined sulfur that contains amorphous sulfur, the residue from the carbon bisulfide extraction is washed with hot aniline until free from sulfur, then with ether until free from aniline, and finally with carbon bisulfide. Occasionally crude sulfur contains a very small amount of amorphous sulfur and must be treated likewise. (See alternate method which can be used.)

tube, dried, cooled and weighed under exactly the same conditions and in the same manner as previously stated.

Calculations.—The weight of the carbon bisulfide insoluble residue remaining in the filter paper divided by three and multiplied by one hundred equals the per cent non-soluble impurities.[35] One hundred per cent minus the above value gives the percentage of sulfur in the sample.

DETERMINATION OF AMORPHOUS SULFUR IN CRUDE SULFUR

Apparatus.—500-ml. Phillips beaker, Whatman's No. 42 filter paper.

Procedure.—Three grams of dried sulfur [36] are extracted with carbon bisulfide in the manner described in the method for the determination of sulfur in crude sulfur.

The filter paper containing the dried residue is removed from the glass weighing tube and placed in a 500-ml. Phillips beaker and treated with 15 ml. of a mixture of two parts bromine and three parts carbon tetrachloride. Shake and allow to stand ten minutes. Add 100 ml. of water containing one gram of sodium carbonate and heat to boiling. Water is added during boiling to keep the volume about 100 ml. When the bromine color becomes very faint, 5 ml. of concentrated hydrochloric acid is added and heating continued until all the bromine is driven off. Filter this solution, heat the filtrate to boiling and precipitate with 10% barium chloride solution. After digesting over night, filter the barium sulfate precipitate off on a No. 42 Whatman filter paper and wash with hot water. Dry and ignite (slowly until paper is burned off) and weigh as $BaSO_4$. If the presence of sulfates is suspected in the original sample, an exact check must be run, omitting only the bromination, to determine the correction.

Calculations.—G. $BaSO_4 \times 13.73 = \%$ amorphous sulfur.

[35] If the sulfur should contain considerable free oil that is soluble in carbon bisulfide, this should be determined and deducted from the total sulfur found. However, with the average grade crude this value is less than one hundredth of one per cent and can be considered negligible.

[36] As sulfur converts rapidly from the amorphous to the crystalline state at drying temperatures this method must be modified slightly to get an accurate result for the actual amorphous sulfur content. That is, by carrying out the carbon bisulfide extraction on an undried sample and determining the moisture content on a separate sample which can be used in correcting results to a dry basis. This factor of the rapid transition of amorphous sulfur to the crystalline form is not recorded in the methods as in determining the sulfur content of a crude sulfur the only important result is usually the total sulfur present.

THE DETERMINATION OF MINUTE QUANTITIES OF FREE OIL IN SULFUR[37]

Apparatus.—Two 250-ml. high form Phillips beakers. Two 300-ml. thin glass beakers, high form, without lip. Two Wiley continuous extractors, without crucible or thimble. Two copper coils prepared by rolling or fluting a sheet of pure copper foil 4″×15″×0.008″ thick in such a fashion that no two points of its surface come into direct contact. It is desirable that the foil be rolled uniformly so that the distance between opposite surfaces shall be approximately 3/16″. The sheet may be cut so that a 3/8″ square tab projects at one corner. A hole punched in the center of this tab provides a convenient method of removing the copper foil from the Wiley tube with a glass hook. The end of the copper foil with the tab should be rolled first so that the tab projects from one end of the roll.

Procedure.—The estimation of oil by simple extraction, as ordinarily made with a volatile solvent, such as diethyl ether or petroleum ether, will not suffice in the case of sulfur, because, while sulfur is only slightly soluble in the solvents, there is usually such a small quantity of oil present (from 0.001% to 0.3%) that the extract contains considerably more sulfur than oil. In this method, extraction is made as usual and the sulfur is removed from the solvent as copper sulfide by refluxing the sulfur contaminated solvent in a Wiley continuous extractor in which has been placed a roll of copper foil.

Fifty grams of the dried sulfur[38] ground to about 60-mesh is weighed and transferred to the 100-ml. flask. On this is poured about 50 ml. of C.P. diethyl ether,[39] the flask is shaken thoroughly at fifteen-minute intervals for a period of one hour. The sulfur is allowed to settle, and the ether is decanted through a filter into the Wiley tube, and a second, smaller quantity of ether is added to the flask, shaken, settled, and filtered as before. The washing is continued in this manner until the sulfur and filter paper are free of oil and the Wiley tube contains approximately 175 ml. of ether, or enough to fill the tube to a level which will cover the copper coil or roll.

The copper coil is cleaned with dilute nitric acid, washed with water, then with alcohol, dried by washing with ether and placed in the Wiley tube. The diethyl ether is then refluxed on a steam or electric bath until all the sulfur has been deposited on the copper coil as copper sulfide.

[37] See Bushnell and Clark, J. Ind. Eng. Chem., 12, 485 (1920).

[38] As the sulfur dried for the moisture determination is practically completely used up in subsequent ash and sulfur determinations an additional 100 grams should be dried simultaneously with the moisture determination whenever free oil is to be determined.

If the free oil content of the sulfur is known to be high it is permissible to use less than fifty grams.

If an accurate determination of free oil on sulfur as received is required this determination should be made on an undried sample, but as free oil is usually determined in order to correct the percentage of sulfur determined by the carbon bisulfide extraction method, both determinations are made on a dried sample due to the fact that if any light oil, volatile at 180° F., were present in the sulfur as received, this might be driven off in the process of drying.

[39] Any diethyl ether which leaves no residue on being evaporated is suitable. In addition to the C.P. grade the U. S. P. for anesthesia grade has been found to be quite satisfactory.

To test for the complete removal of sulfur the copper coil is removed from the tube after being washed with ether and cleaned as before with nitric acid, water, alcohol and ether. The coil is then replaced in the Wiley tube and refluxing continued. The ether is free of sulfur when no darkening of the freshly cleaned copper coil is observed after refluxing has continued for thirty minutes.

When the ether is free of sulfur it is transferred to a weighed beaker after being filtered to remove the portion of copper sulfide which flakes off of the coil during the course of the removal of the sulfur as copper sulfide. The copper coil, Wiley tube and filter paper are washed with small quantities of diethyl ether until this apparatus is free from oil. These washings are also added to the weighed beaker and the whole is gently evaporated to constant weight at a low temperature (150°–200° F.).

Calculations.—The weight of the oil extracted in grams (gain in weight of the beaker) multiplied by two equals the percentage of free oil contained in the sulfur.

THE DETERMINATION OF MOISTURE IN SULFUR

Apparatus.—Flat bottomed glass petri dish (diameter 95 mm., height 15 mm.).

Procedure.—Fifty grams of the sulfur sample ground to 4-mesh or less are weighed into a tared petri dish and placed in a drying oven, regulated to a constant temperature of 82.2° C. (180° F.) [40] and *dried to constant weight.* Drying overnight (12 to 18 hours) is usually sufficient time to dry completely the sample. At the end of the drying period the dish is removed from the oven, placed in a desiccator to cool, and is carefully weighed after having reached room temperature.

Calculations.—Loss in weight in grams multiplied by two equals the percentage moisture in the sample.

[40] It has been found that more accurate results are obtained by drying samples for rather a long period of time at a comparatively low temperature than to dry for a shorter period at higher temperatures. This is due to the fact that at temperatures as low as 100° C. (212° F.) a very slow sublimation of sulfur will occur.

DETERMINATION OF ASH IN SULFUR

Apparatus.—No. 1 low form porcelain crucible.

Procedure.—Twenty-five grams of finely ground, dried sulfur [41] is weighed into the tared crucible and placed on a hot plate. The heat of the hot plate is controlled so that the sulfur burns slowly, but completely. After the sulfur has completely burned off, the crucible is ignited in an electric muffle furnace to constant weight (twenty to thirty minutes at approximately 1500° F. is usually sufficient). The crucible is cooled to room temperature in a desiccator and weighed.

Calculations.—The weight of the residue in grams (gain in weight of the crucible) multiplied by four equals the percentage of ash present in the sulfur.

DETERMINATION OF ACIDITY IN SULFUR

Apparatus.—Two 250-ml. Erlenmeyer flasks.

Procedure.—Twenty grams of the undried sample are ground to approximately 60-mesh, and placed in a 250-ml. Erlenmeyer flask. The sulfur is then moistened with 25 ml. of ethyl alcohol and agitated for several minutes; 50 ml. of distilled water are added and the flask again agitated and allowed to stand for thirty minutes with occasional shaking. The contents of the flask are then titrated with N/50 sodium hydroxide using phenolphthalein as an indicator. A blank is run on the alcohol-water mixture, simultaneously with the sample, and its titration subtracted from that of the sample.

Calculations.—The acidity is calculated to percentage of sulfuric acid according to the following formula:

$$\text{ml. N/50 NaOH} \times 0.004904 = \%\ H_2SO_4.$$

[41] The dried sample from the moisture determination is usually and preferably used.

THALLIUM [1]

Tl, *at.wt.* 204.39; *sp.gr.* 11.85; *m.p.* 303° C.; *oxides* Tl_2O, Tl_2O_3.

Occurrence.—Thallium occurs in quantity only in a few rare minerals, such as crookesite, $(Cu, Tl, Ag)_2Se$, and lorandite, $TlAsS_2$. It is usually found in small quantities in association with the alkali metals, zinc, iron, and lead, and is obtained from the flue dust formed in the calcination of iron pyrites and lead ores.

Uses.—The chief use of thallium appears to be in the manufacture of rat and vermin poison, as the metal and its compounds are extremely toxic. It is further used in the preparation of artificial stones and optical glass of very high refracting power.

Behavior in Solution.—Thallium forms two series of salts. In thallous salts the metal is univalent and, while showing distinct affinities with the alkali metals, furnishes reactions recalling those of lead; thallous sulfate, hydroxide, chloroplatinate, and cobaltinitrite resemble the respective potassium salts, but thallous chloride, iodide, sulfide, and chromate are precipitated in an analogous manner to the corresponding lead compounds.

Thallic salts are formed by oxidation of thallous salts with chlorine, permanganate, or some other oxidizing agents; they resemble ferric salts in being readily hydrolyzed, yielding brown basic salts, and giving a brown gelatinous precipitate with ammonia.

DETECTION

In systematic qualitative analysis, thallium is found in the zinc-nickel group, being precipitated by ammonium sulfide from ammoniacal solution.

The solution to be tested is evaporated with sulfuric acid to eliminate lead, the filtrate saturated with hydrogen sulfide, and the precipitate filtered off. The filtrate is freed from hydrogen sulfide by boiling, and oxidized with nitric acid. Iron, aluminum, the zinc-nickel group, and the alkaline earths are next precipitated from boiling solution with sodium carbonate, and removed by filtration. The filtrate is treated with ammonium sulfide; if a brown precipitate is formed, it is collected, dissolved in a little sulfuric acid, and the boiled solution treated with potassium iodide. A yellow crystalline precipitate proves the presence of thallium. The precipitate, tested in the loop of a platinum

[1] Chapter by W. R. Schoeller, Ph.D., and A. R. Powell, Metallurgical Chemists, London, England.

wire in the Bunsen flame, gives a characteristic brilliant green flame which, viewed through the spectroscope, shows a broad green line at 5350.7.

PREPARATION OF SOLUTION

Practically all materials containing thallium yield it to treatment with hydrochloric acid, nitric acid, or aqua regia. Glasses and artificial stones must, however, be fused with sodium carbonate, the melt being taken up in water. However obtained, the solution is evaporated with sulfuric acid until copious fumes are evolved; the cold mass is dissolved in water and the solution filtered for the removal of lead sulfate. If the amount of thallium present is very small, a large amount should be taken for analysis; after expulsion of nitric by means of sulfuric acid, the solution (filtered if necessary) is boiled with strips of zinc until effervescence ceases and basic salts begin to be precipitated. A few ml. of hydrochloric acid are added, and the solution filtered while a feeble evolution of hydrogen from the zinc is maintained. The precipitate is collected, washed, digested with hot 20% sulfuric acid, and the solution containing the thallium filtered.

SEPARATIONS

1. **General Method.**—The sulfate solution, obtained by one of the above methods, is neutralized with sodium carbonate, 5 gms. of potassium cyanide and a further 2 gms. of sodium carbonate added, and the mixture warmed on the water-bath. The precipitate is filtered off and washed with a one per cent solution of sodium carbonate. To the filtrate, which contains all the thallium, are added a few ml. of colorless ammonium sulfide; the precipitated thallous sulfide is collected, washed with a very dilute solution of ammonium sulfide, dissolved in a minimum of hot 10% sulfuric acid, the solution boiled to expel hydrogen sulfide, and the thallium estimated as iodide or chromate (see below).

2. **Special Methods.**—(*a*) *From Ferric Iron, Aluminum, and Chromium.*[2]—The sulfuric acid solution is approximately neutralized with sodium carbonate, treated with 20 ml. of 7% ammonium nitrite solution at 40° C. followed by 20 ml. of methyl alcohol, and gently boiled for twenty minutes. The precipitate is left to settle, collected, and washed with dilute ammonium nitrate solution. Complete precipitation is ascertained by a small addition of the reagents to the filtrate and further short boiling. The filtrate is evaporated to 100 or 200 ml., made ammoniacal, and the thallium precipitated as chromate (see below).[3]

[2] Moser and Reif, Monatsh. Chem., 52, 343 (1929).
[3] Moser and Brukl, Monatsh. Chem., 47, 709 (1926).

(*b*) *From Zinc, Cadmium, Nickel, Cobalt.*[3]—The acid solution, warmed to 60° C., is treated with ammonia until the precipitate has re-dissolved, when a decided excess of ammonia is added. The thallium is then precipitated as chromate (see below).

GRAVIMETRIC ESTIMATION

(a) As Chromate.—This procedure is recommended as the most accurate by Moser and Brukl.[3] Thallous chromate, Tl_2CrO_4, is soluble to the extent of 0.006 gm. per liter of solution containing 2% of ammonia, 4 of potassium chromate, and 10 of alcohol. The acid sulfate solution is made ammoniacal, boiled, and stirred during additions of potassium chromate solution, the excess of which should yield an approximately 2% solution. The yellow precipitate is allowed to stand for twelve hours, filtered by decantation on a porous crucible, washed with 1% chromate solution, then 50% alcohol, dried at 120° C., and weighed. Factor for Tl, 0.77895.

(b) As Iodide.—The sulfate solution (less than 100 ml.), if acid, is neutralized with sodium carbonate, and treated at 80° C. with a 10% potassium iodide solution drop by drop until no further precipitate forms; one gm. of solid iodide is then added in excess. The precipitate is allowed to stand overnight, collected in a porous crucible, washed first with a minimum quantity of cold 1% potassium iodide solution, then with 80% alcohol until the washings cease to react for iodide, dried at 110° C., and weighed. Factor for Tl, 0.6169.

VOLUMETRIC ESTIMATION[4]

Thallous sulfide, obtained as described under "Separations, 1," is dissolved in 4 ml. of hydrochloric acid and a little water. The solution is boiled to expel hydrogen sulfide, cooled, diluted to 60 ml., and titrated with 0.1N permanganate solution standardized against pure thallous chloride.[5]

[4] Flawky, J. Am. Chem. Soc., 29, 300 (1907).

[5] Ceric sulfate may be used in the titration. For 0.1–0.3 g. Tl the solution should contain 10–30 ml. HCl and be titrated at 50°. ICl may be used as catalyst, Willard and Young, J. Am. Chem. Soc., 52, 36 (1930). See chapter on Standard Solutions.

ESTIMATION IN RAT POISON[5]

The paste or ground grain (5 gms.) is heated with 100 ml. of nitric acid and 10 of sulfuric acid in a Kjeldahl flask till the nitric acid is expelled; sodium nitrate is added in small portions till the solution is colorless or pale yellow. The solution is diluted to 70 ml., and boiled; 2.5 ml. of 6% sulfurous acid is added for the reduction of any thallic sulfate formed, and the sulfur dioxide boiled off. The liquid is neutralized with ammonia against rosolic acid. The contents of the Kjeldahl flask are transferred to a 200-ml. flask, 5 ml. of glacial acetic acid being added. After adjustment of the volume, 100 ml. of filtrate are heated to 90° C. and the thallium precipitated with 25 ml. of 4% potassium iodide solution. The precipitate is collected, washed, and treated as above, 80% acetone being substituted for the alcohol.

[5] Lepper, Z. anal. Chem., 79, 321 (1930).

THORIUM[1]

***Th**, at.wt.* **232.12**; *sp.gr.* **11.0–12.2**; *m.p.* **1450°**; *oxides* **ThO_2** **(ThO_3** *and* **Th_2O_7** *known only in hydrate form*)

The main source of thorium is monazite sand, of which the greater part comes from Brazil and India. The South Carolina monazite is of poor quality and of very little commercial importance. Monazite is essentially an orthophosphate of the cerium earths, and carries from about 4% to nearly 10% of ThO_2. The highest grade material comes from Travancore, India. Thorite and thorianite, the silicate and the uranate respectively of thorium, are now of limited importance. The greater part of all thorium coming into the market is converted to thorium nitrate for use in the incandescent gas mantle industry, the average mantle consisting of about 99% ThO_2.

DETECTION

In the regular analytical procedure thorium is found in the precipitate of the tri- and tetravalent hydroxides produced by ammonium hydroxide, provided a sufficiently thorough decomposition of the sample has been obtained (see section on preparation and solution of sample). Along with rare earth elements, and a little zirconium, thorium may be obtained as oxalate by dissolving the hydroxide precipitate[2] in hydrochloric acid and adding a slight excess of oxalic acid to the hot, weakly acid (not over 0.5 normal) solution. The precipitate should be allowed to stand six or eight hours before filtration. After having been washed with water containing 2 ml. of 6 normal hydrochloric acid per 100 ml., the precipitate is rinsed into a beaker with pure water, using about 50 ml. To this mixture 5 g. of solid ammonium oxalate are added, and the mixture is heated for half an hour nearly to boiling, and well stirred. Two volumes of water are added, the mixture is allowed to stand half an hour and then filtered. To the filtrate 20 ml. of 6 normal hydrochloric acid

[1] By Paul H. M.-P. Brinton.

[2] It is shorter to add oxalic acid directly to the filtrate from the hydrogen sulfide group, after boiling out the excess of hydrogen sulfide. This, however, causes complications in the analysis of subsequent groups, and may also contaminate the oxalate precipitate with calcium; so it is better first to precipitate the hydroxides with (carbonate-free) ammonium hydroxide as described.

are added. A white precipitate indicates the presence of thorium.[3] This precipitate can be put into solution by strong heating with concentrated sulfuric acid, and taking up with ice-cold water. One of the following characteristic tests may be used as confirmation of thorium.

A sensitive test for thorium [4] consists in the precipitation of thorium iodate in nitric acid solution. Two reagent solutions are necessary: (I) 15 g. of potassium iodate, 50 ml. of concentrated nitric acid, and 100 ml. of water. (II) 4 g. of potassium iodate, 50 ml. of concentrated nitric acid, and 450 ml. of water. The solution to be tested for thorium, which must contain no hydrochloric acid, is boiled with a little sulfurous acid to reduce any cerium present. To this solution is added twice its volume of reagent (I), which causes precipitation of thorium iodate, and more or less rare earth iodates according to their concentration in the solution. By now adding reagent (II) in volume equal to four times the original volume, and boiling, any rare earth iodate is dissolved, while thorium iodate (also any zirconium iodate) remains undissolved. If the absence of zirconium is not known with certainty, the iodate precipitate may be boiled with 50 ml. of 10% oxalic acid solution [5] until iodine vapors are no longer given off. Any precipitate remaining is thorium oxalate.

Sodium pyrophosphate produces in solutions of an acid normality of 0.2–0.3 a white precipitate of thorium pyrophosphate. To make certain that this precipitate is entirely free from rare earths it should be redissolved, any tetravalent cerium reduced with sulfurous acid, and then the thorium reprecipitated as pyrophosphate as described later under Gravimetric Determination. Zirconium and titanium would also be precipitated under these conditions, but they would be separated from thorium on the basis of their non-precipitation by excess of oxalic acid.

Spectrum analysis, and the determination of radioactivity [6] are also useful in the detection of thorium.

[3] Thorium oxalate is soluble in ammonium oxalate. Zirconium oxalate, and traces of the oxalates of the yttrium earths also dissolve, but the yttrium earth oxalates are reprecipitated on dilution. The addition of an excess of mineral acid to the ammonium oxalate solution of thorium and zirconium precipitates thorium oxalate, but not zirconium oxalate.

[4] Meyer and Hauser, "Die Analyze der Seltenen Erden und Erdsaüren," p. 171. Ferdinand Enke, Stuttgart (1912).

[5] Brinton and James, J. Am. Chem. Soc., 41, 1084 (1919).

[6] Helmick, J. Am. Chem. Soc., 43, 2003 (1921), gives details for the quantitative, as well as the qualitative, determination of thorium in minerals.

ESTIMATION

The compounds of thorium are as a rule very difficultly soluble and even those considered soluble in a given solvent are apt to be rather slowly soluble, so patience must be frequently exercised or thorium will be partially or wholly passed over, being counted as insoluble residue. In the regular procedure thorium, if not specifically looked for, will be counted as aluminum, if the latter is taken by difference from the ammonium hydroxide precipitate.

PREPARATION AND SOLUTION OF THE SAMPLE

Thorite.—The very finely pulverized sample is digested with concentrated hydrochloric acid at a temperature just below boiling. This usually effects complete decomposition, but for safety any insoluble residue should be filtered, after dilution, ignited, and then fused with potassium pyrosulfate. This fusion is taken up with 6 normal hydrochloric acid and added to the main solution. Silica and the hydrogen sulfide group are removed in the conventional way, leaving thorium, rare earths, etc., in the acid solution.

Monazite, Thorianite, Gas Mantle Residues, etc.—While fusion with potassium pyrosulfate effects the decomposition, yet it is more convenient to attack larger samples with concentrated sulfuric acid. In the case of monazite sand, large samples are necessary to insure uniform and representative samples. Thorianite and Carolina monazite should be finely ground, but Brazilian and Indian monazite are fully decomposable without grinding, and filtration from the insoluble residue is easier if the sample is taken as it comes. A batch of sand should be very carefully mixed before sampling, to avoid the tendency toward segregation arising from the different sizes and densities of the constituent grains.

The following method for the decomposition of monazite is recommended by Dr. H. S. Miner,[7] of the Welsbach Co.: 50 g. of the sand are weighed out and placed in a porcelain casserole of about 500 ml. capacity. Seventy-five ml. of concentrated sulfuric acid are added, and the mixture is heated for about four hours with frequent stirring, a gentle evolution of fumes being maintained during the course of the operation. When the mass has become pasty, it is allowed to cool, and the sulfates are extracted by the addition of about 400 ml. of ice-cold water, or enough to cool the solution sufficiently so that the sulfates become soluble. This solution is decanted into a liter-graduated flask, and the remaining sulfates are extracted with small portions of cold water and decanted into the flask. A point is reached toward the end of the extraction when, due to the decreasing acidity, the small wash portions show a slight separation of rare earth phosphate. A few more extractions are made beyond this point, but these portions are not added to the graduated flask. They are temporarily preserved in a separate beaker. To the remaining sand, which has been dried, 10 ml. of concentrated sulfuric acid are added, and the digestion is carried out as before, except that a somewhat higher temperature is used, enough to maintain copious evolution of white fumes, and the duration of the digestion need not exceed one and a half hours. After cooling, extraction

[7] U. S. Bureau of Mines, Bulletin 212, p. 53 (1923).

is started with the last portions of the previous extraction liquor, i.e., those decanting which showed slight precipitates of rare earth phosphates, and which were preserved in the separate beaker. The sand is now thoroughly washed with cold water, and the washings are all decanted into the liter flask. This flask now contains all the thorium and rare earths as soluble sulfates. A little suspended silica is usually visible at this point, but this will not be mistaken for undissolved sulfates.

After cooling, the sulfate solution is made up exactly to the liter mark, thoroughly mixed, and filtered through a dry filter, discarding the first 25 or 30 ml., and receiving the remainder in a dry flask or bottle. The whole need not be filtered, and, of course, no washing is to be done. Each 100 ml. of this solution represents 5 g. of the sample.

SEPARATIONS

Thorium is separated from practically all elements excepting the rare earth elements and scandium by precipitation as oxalate in slightly acid solution. Zirconium may be in part precipitated along with thorium and the rare earths, especially in the absence of a sufficient excess of oxalic acid; and if considerable quantities of calcium, and to less extent strontium and barium, are present, there may be contamination unless the mineral acid concentration be kept dangerously high. In the presence of much calcium, it is better first to separate thorium from it by precipitation with freshly distilled ammonium hydroxide, and then to precipitate the thorium as oxalate. The details of the oxalate separation have been given under Detection.

The main problem, then, is the separation of thorium from the rare earth elements. The iodate method has already been given in detail. Three other satisfactory methods will now be described.

The Pyrophosphate Method.[8]—An aliquot portion of the sulfate solution, prepared as already described, and usually representing 2.5 g. of monazite sand, is diluted to about 450 ml., and 5 ml. of concentrated hydrochloric acid are added. The solution is heated nearly to boiling and the iron and cerium are reduced by adding sulfurous acid solution until the yellow color is discharged. Fifteen ml. of sodium pyrophosphate solution (50 g. $Na_4P_2O_7 \cdot 10H_2O$ in 1 liter of water) are slowly added, with constant stirring, and the mixture is then heated to gentle boiling for 5 minutes. After standing 5–10 minutes—not more—the precipitate of thorium phosphate is filtered and washed twice with water containing 1 drop of hydrochloric acid per 100 ml. A slight cloud in the first filtrate, due to atmospheric oxidation of iron (and possibly of cerium), with consequent precipitation of pyrophosphate may be neglected.[9] The filter paper and precipitate are freed from excess liquid by wrapping for a moment in cheap filter paper or blotting paper, and then dropped into a dry 250-ml. Kjeldahl flask. Fifteen ml. of concentrated sulfuric acid and a few crystals of ammonium perchlorate are added, a small funnel is placed in the neck of the flask, and the contents are heated until the filter is disintegrated.

[8] Carney and Campbell, J. Am. Chem. Soc., 36, 1134 (1914).
[9] V. T. Jackson, U. S. Bureau of Mines, Bulletin 212, p. 65 (1923).

When a clear brown solution is obtained more perchlorate [10] is added, and the heating is continued until the mixture is pure white (or very slightly yellow if much cerium was carried down in the first precipitate). The flask is placed in ice-water and then slowly, with shaking, about 100 ml. of ice-cold water are added. Complete solution may at times require several hours. Occasionally a slight cloud of suspended silica persists. This may be neglected as it will be removed in the next step.

The sulfate solution is rinsed into a solution of 30 g. of sodium hydroxide in 125 ml. of water, contained in the original beaker in which the pyrophosphate was precipitated,[11] boiled for several minutes, filtered and washed several times with hot water. The paper and precipitate are then placed in the beaker just used, 10 ml. of concentrated hydrochloric acid are added, and after a few minutes of stirring, 150 ml. of water are added, and the solution is boiled. The paper shreds are filtered off and washed, and the filtrate is diluted to about 400 ml. Three ml. of saturated sulfurous acid solution are added, the solution is heated to boiling, and the thorium is again precipitated with sodium pyrophosphate. The precipitate is washed and changed to sulfate and hydroxide in the manner just described. This second sulfate should always be perfectly white, and should dissolve entirely clear. The final hydroxide is free from rare earths, and aside from zirconium and titanium, which are precipitated as pyrophosphate, it should contain only a trace of iron as impurity. These three foreign elements will be separated from the thorium by the final precipitation of the latter as oxalate. The last hydroxide precipitate is dissolved in as little concentrated hydrochloric acid as possible (never more than 15 ml.) and filtered free from paper. This chloride solution is now ready for the gravimetric determination of thorium by precipitation as oxalate.

The Thiosulfate Method.[12]—Two hundred ml. of the sulfate solution prepared as described under Preparation of Sample, and representing 10 g. of monazite sand, are diluted to 1 liter, and poured into 150 ml. of a cold saturated solution of oxalic acid. The sulfate solution should be fed in very slowly, preferably from a separatory funnel, and vigorous stirring should be maintained to convert the gummy precipitate to the crystalline form. Only in this way is it possible to get the oxalate precipitate free from considerable amounts

[10] The oxidation of the filter paper requires 10 or 15 minutes, and about 1.5 g. of perchlorate. Heating should not be continued far beyond the point at which the organic matter is fully destroyed, as the perchloric acid may break up and cause considerable foaming. Cartledge (J. Am. Chem. Soc., 41, 49, 1919) shows that fuming nitric acid may be satisfactorily substituted for ammonium perchlorate. In this case the precipitate and paper are shaken with 15 ml. of concentrated sulfuric acid in the Kjeldahl flask for about two minutes, cooling, if necessary, until the flask is just a little too hot to be held comfortably in the hand. To the charred mixture 2–4 ml. of fuming nitric acid (sp.gr. 1.53) are added, and after a minute or two the solution is gradually raised to the boiling point. Occasionally as fumes of sulfur trioxide appear a second charring occurs, in which case 0.5 ml. more nitric acid, poured cautiously down the neck of the flask, will complete the oxidation. (If the mixture has once been white or slightly yellow, no harm is done if during cooling oxides of nitrogen redissolve in the acid, thereby restoring a yellow color.)

[11] Thorium pyrophosphate adheres rather tenaciously to the glass, and this procedure eliminates the necessity for the tedious cleansing of the beaker after the first precipitation.

[12] The details here given are essentially those in use in the laboratories of the Welsbach Co. See H. S. Miner, loc. cit.

of phosphate. After standing not less than fifteen hours the precipitate is filtered, washed free from acid, and dried.

The filtrate and first washings are neutralized with ammonia, and hydrochloric acid is then added in an excess of from 10 to 15 ml. This precipitates the remaining rare earths (and any thorium still in solution) as oxalo-phosphates. This precipitate is also allowed to stand fifteen hours, and then it is filtered and washed with weak oxalic acid solution. This precipitate, after drying, is ignited in a porcelain dish, moistened with a little water, and dissolved by warming with concentrated hydrochloric acid. The solution so obtained is filtered, largely diluted, and precipitated by the addition of a large excess of oxalic acid, warming to convert the precipitate to a crystllaine form. After standing two or three hours, this oxalate precipitate is filtered, washed, and dried.

The oxalate precipitates are ignited together. If " total rare-earth oxides " are wanted, they may be weighed at this point. The oxides are transferred to a 600-ml. beaker, moistened with a little water, and dissolved by warming with 100 ml. of 6 normal hydrochloric acid. The solution is transferred to a 1500-ml. beaker, diluted to about 700 ml., and ammonia is added until the precipitate formed just ceases to redissolve, leaving the solution neutral or very slightly acid. Concentrated hydrochloric acid is now added, a drop at a time, until the precipitate just dissolves, and then 6 to 8 drops more. One hundred ml. of a boiling 30% sodium thiosulfate solution are added to the boiling solution, and boiling is continued for 45 minutes. The precipitate is filtered on a 2¼-inch Büchner funnel, and washed with hot water. It is well to fold the filter paper so as to cover the whole of the inside of the funnel.

To the filtrate 10 ml. more of the thiosulfate solution are added, and it is boiled for half an hour longer. The small precipitate thus obtained is filtered, set temporarily aside and designated as " Residue No. 1." The filtrate is discarded.

The paper containing the first large precipitate is put into the original 1500-ml. beaker and boiled over a low flame with 75 ml. of 6 normal hydrochloric acid. When the thorium precipitate has dissolved and the paper is pretty well disintegrated, usually about 5 minutes, without filtering off the filter paper and sulfur, the mixture is diluted to 700 ml., and neutralized with ammonia just as before, finally having an excess of 6 to 8 drops of concentrated hydrochloric acid. It is then heated to boiling and 60 ml. of boiling 30% sodium thiosulfate solution are added. After boiling 30 minutes the precipitate is filtered on a Büchner funnel as before and washed. This filtrate is reserved.

The paper and precipitate are dropped into the original beaker and all the operations described in the paragraph immediately preceding are repeated, the final filtrate, however, being this time discarded.

The paper containing the thorium precipitate is boiled with 40 ml. of 6 normal hydrochloric acid. When the paper is well disintegrated, it is filtered off, well washed, and this residue is designated as " Residue No. 2." The solution is temporarily set aside.

Residues Nos. 1 and 2 are combined, ignited in a porcelain crucible, and fused with sodium pyrosulfate. The fusion is extracted with dilute hydro-

chloric acid and this solution is added to the reserved filtrate from the second thiosulfate precipitation. Ammonia is now added in excess, the precipitate is filtered, and dissolved in hydrochloric acid. This solution is diluted to 300 ml. nearly neutralized with ammonia, leaving only a faint acidity, heated to boiling, and precipitated by the addition of 20 ml. of boiling 30% sodium thiosulfate solution. After boiling 20 minutes, the precipitate is filtered on a small Büchner funnel, washed, and dissolved in 50 ml. of 6 normal hydrochloric acid. Without filtering, the solution is diluted to 300 ml., almost neutralized with ammonia, and the thiosulfate precipitation is repeated. The last precipitate is dissolved by boiling in a mixture of 5 ml. of concentrated hydrochloric acid and 20 ml. of water, the sulfur is filtered off, and the chloride solution is combined with the solution obtained at the end of the preceding paragraph.

This solution now contains all the thorium from the original sample and it is ready for the Gravimetric Determination of thorium by precipitation as oxalate.

The Phenylarsonic Acid Method.[13]—To a 100-ml. portion of the sulfate solution, prepared as described under Preparation and Solution of the Sample, and representing 2.5 g. of monazite sand, 15 ml. of concentrated nitric acid are added, and this solution is poured into a hot solution of 10 g. of oxalic acid. After standing six or more hours the oxalate precipitate is filtered, washed, and then decomposed by boiling with 25 ml. of concentrated nitric acid. Heating is continued until the volume of the solution has been reduced to about 15 ml., after which 10 g. of oxalic acid in hot solution are added and the whole is diluted to about 200 ml. After again allowing to stand for several hours the precipitated oxalates are filtered, washed, and once more decomposed by concentrated nitric acid, the final evaporation this time being carried almost to dryness. Three hundred ml. of water are now added, and the cerium is reduced to the cerous condition by the addition of sulfurous acid.

The boiling solution, now practically free from phosphoric acid and containing all the thorium and rare earth elements, is treated with 30 ml. of a 10% solution of phenylarsonic acid [14] and 75 ml. of acetic acid. This is followed by the slow addition of a concentrated solution of ammonium acetate until it is evident that all thorium phenylarsonate has been precipitated. After digestion for ten minutes on the hot plate the thorium phenylarsonate, slightly contaminated by rare-earth compounds, is filtered, washed, and then dissolved in 30 ml. of 1 : 1 hydrochloric acid, the solution being next diluted to about 300 ml., and treated with a little sulfurous acid to insure the reduction of any cerium present. The thorium phenylarsonate is now reprecipitated by the addition of a few ml. of phenylarsonic acid, 75 ml. of acetic acid, and enough ammonium acetate to insure complete precipitation. This precipitate is filtered, washed, and then dissolved in 1 : 1 hydrochloric acid, and the solution is then ready for the gravimetric determination of thorium by precipitation as oxalate. To insure the absence of arsenic in the thorium dioxide finally weighed it is well to add 5 g. of solid oxalic acid to the 1 : 1 hydrochloric acid solution

[13] Rice, Fogg and James, J. Am. Chem. Soc., 48, 895 (1926).
[14] This reagent may be readily prepared by the method of Palmer and Adams, J. Am. Chem. Soc., 44, 1361 (1922).

of the last phenylarsonate precipitate, and then to dilute to about 200 ml., and allow to stand twelve hours before filtering.

GRAVIMETRIC DETERMINATION OF THORIUM

Thorium is nearly always precipitated as oxalate and ignited to ThO_2, in which form it is weighed. The solubility of thorium oxalate in very dilute mineral acids is slight, especially in the presence of excess oxalic acid. It is well, however, not to have over 3 ml. of concentrated mineral acid per 100 ml. of solution. More strongly acid solutions may be partially neutralized with ammonium hydroxide. Thorium oxalate does not filter readily if precipitated rapidly, or from a cold solution. The solution should be boiling hot and dilute (200–500 ml.); and should be precipitated by adding very slowly a boiling-hot solution of oxalic acid, which has been saturated in the cold; or by stirring in the oxalic acid added in solid form. Both methods insure a slow rate of precipitation, but the first method seems to be the better. The precipitate is allowed to stand not less than 10 or 12 hours before filtration, and it is washed with water containing a few drops of hydrochloric acid and a little oxalic acid.

The thorium oxalate is ignited with the filter paper in a porcelain or platinum crucible over the blast to constant weight. If a platinum crucible is used, the full heat of a Meker burner is sufficient. The ThO_2 finally weighed should be pure white in color. A yellow color shows cerium earths or iron and is an indication of faulty work.

Recommended Method for the Determination of Thorium in Monazite Sand.—Fifty g. of the well mixed sand, unground if of Brazilian or Indian origin, are decomposed by sulfuric acid as described under Preparation and Solution of the Sample, and diluted to exactly 1 liter. Fifty ml. of this solution are carefully pipetted off, and separated from the rare-earth elements by the pyrophosphate method as given under Separations. The hydrochloric acid solution so obtained, containing from 10 to 15 ml. of concentrated acid, is diluted to about 500 ml., and the thorium precipitated as oxalate as described under Gravimetric Determination, ignited, weighed, and reported as ThO_2.

References for Special Determinations

Survey of methods for the detection and determination of small amounts of thorium, W. Singleton, Ind. Chem. Manuf., 2, 454 (1926).
The determination of thorium in tungsten filaments, Brophy and Van Brunt, J. Ind. Eng. Chem., 19, 107 (1927); P. Selenyi, Z. anorg. allgem. Chem., 160, 318 (1927).
The determination of thorium in radio-active minerals for estimation of geologic age, C. N. Fenner, Am. J. Sci., V, 16, 369 (1928); Gladys D. Finney and R. D. Evans, Phys. Rev., 48, 503 (1935).

TIN[1]

Sn, *at.wt.* **118.7;** *sp.gr.* **6.56;** *m.p.* **232°;** *b.p.* **2275°;** *oxides* **SnO_2** *and* **SnO**

Introductory Notes.—Tin occurs native to a very limited extent. It occurs as sulfide and extensively as oxide. It is found combined in silicic rocks such as granite, etc. It occurs in small amounts in feldspars, columbates, ilmenite, tantalate. The mineral cassiterite (stream tin, tin stone) is of commercial importance and the chief source of tin. The mineral stannite (tin pyrites), $Cu_2S \cdot FeS \cdot SnS_2$, is another source of less importance.

DETECTION

Hydrogen Sulfide precipitates, from dilute acid solutions, SnS, brown or SnS_2, yellow, according to the valence of the tin ions in solution. The sulfides are soluble in yellow ammonium sulfide (distinction from sulfides of Hg, Pb, Bi, Cu and Cd). The sulfides will not precipitate in a concentration of 1 : 4 HCl (sp.gr. 1.19) (distinction from Sb and As sulfides). The sulfides are easily soluble in concentrated HCl (distinction from As sulfides).

Mercuric Chloride is reduced to white HgCl, or gray Hg and HgCl by addition of stannous chloride solution. In the usual procedure of detection tin is precipitated from dilute HCl or H_2SO_4 solutions as sulfide by H_2S (2.5 ml. HCl or 1.5 ml. H_2SO_4 per 40 ml., later diluted to 100 ml. and again saturated with H_2S). It is separated from the sulfides of Hg, Pb, Bi, Cu and Cd by extraction with ammonium polysulfide. It is precipitated from the extract by acidification (filter). It is separated from As sulfide by extraction with concentrated HCl. The extract is filtered from As sulfide, tin reduced by addition of metallic iron wire, or granulated lead[2] or aluminum foil[3] and the

[1] In the early periods tin was thought to be identical with lead, but during the period of Pliny (23–79 A.D.) a distinction was recognized between these metals. The metal was brought to Egypt and Greece by the Phoenicians from the British Isles (Cassiterides). Tin is used as a coating for iron in the manufacture of numerous articles for industrial and domestic use. Block tin pipes are used for conveying distilled water. Tin foil for wrapping material. Tin is a constituent of a number of alloys such as Babbitt metal (Sn, Cu, Sb), bronze (Sn, Cu), pewter (Sn, Pb), solder (Sn, Pb), and type metal (Sn, Pb, Sb). Tin compounds are used in the arts and industries.

[2] The tin solution may be passed through a column of granulated lead.

[3] A tin mineral placed on a piece of zinc in dilute HCl will coat the zinc with gray metallic tin. If Al is used a piece of foil 1/32″×¼″×1″ is recommended. This dissolves completely and makes it possible to detect 1 mg. of Sn in presence of 500 mg. or Sb and As.

reduced solution added to an excess of $HgCl_2$ solution; a white precipitate of HgCl, insoluble in dilute (1 : 2) HCl proves the presence of tin (SbOCl dissolves).

ESTIMATION

The estimation of tin is required in connection with the analysis of tin ores, dross, ashes, dust, tin plate, alloys such as solder, canned foods, and general analysis.

In analyses should provision not be made for tin, loss of this element will occur by volatilization during the attack of the ore in its decomposition and solution. Owing to hydrolysis some of the element will remain as an oxide with silica causing an error in the silica determination. The portion still remaining in solution will precipitate with the NH_4OH precipitate causing an error in the determination of aluminum. Due to its complete reduction to metallic state it does not interfere with the volumetric determination of iron when zinc is used as a reducing agent.

In the decomposition of the material special precautions must be observed to prevent the loss of tin due to volatilization. H. B. Knowles found that no loss occurs if dilute hydrochloric acid solutions are boiled in covered beakers or when H_2SO_4 is present with the HCl with evaporation to fumes.[4] Chlorides especially $SnCl_4$ volatilize on evaporation.

Decomposition of the silicate ores may be effected by fusion with NaOH, or Na_2O_2 or with a mixture of Na_2CO_3, K_2CO_3 and S. Minerals are first extracted with dilute HNO_3 followed by fusion of the insoluble residue.

OPENING UP TIN ORES

As the oxides of tin are not readily soluble in acids the tin can be most easily removed by assay. Ores, slags, dross, and ashes are first subjected to the assay process. The button obtained is then analyzed either volumetrically or gravimetrically by one of the methods given below. Having the weight of the button and the per cent of tin in it, the per cent of tin in the sample as received can be calculated. Consult the "Introductory" paragraphs.

There are two general processes of assaying, namely, the Cyanide Process and the Carbonate of Soda Process.

THE CYANIDE PROCESS

The theory of this method is that the oxides are reduced to the metal by the action of potassium cyanide, the reaction being represented as follows:

$$SnO_2 + 2KCN = Sn + 2KCNO.$$

[4] Applied Inorganic Analysis—Hillebrand and Lundell, John Wiley and Sons.

Potassium cyanide reduces other metals also, so that the button obtained is not pure.

Procedure.—Take 100 grams of the sample which has been dried and finely powdered. (For complete analysis the moisture should be determined in the usual way.) Mix thoroughly with four times its weight of powdered potassium cyanide. Place about 1 in. of potassium cyanide in the bottom of a number H (height 5⅞ ins., diameter 3¾ ins.) Battersea clay crucible. Place the mixture of sample and cyanide on top of the cyanide in the crucible and cover with enough more cyanide to fill the crucible to within 1 in. of the top.

Place the crucible in the assay furnace and heat slowly until it has been thoroughly warmed and the cyanide begins to melt. Then increase the heat gradually to a pure white, taking care that the cyanide does not boil over.[5] Grasp the crucible with the tongs and tap it gently on the hearth to assist in settling the metal. Continue the heating until all of the organic matter has disappeared, adding more cyanide from time to time if necessary. Near the end of the process the molten mass becomes clear and transparent and finally pasty and translucent. When this last condition appears, remove the crucible from the furnace and allow it to cool slowly at the temperature of the room.

When cool, break the crucible and slag away from the button. The appearance of the button and the slag immediately surrounding it indicates whether or not the process has been properly manipulated. The button itself should be firm and compact and the slag around it should be white or greenish in color. If the button is spongy or if the slag has a dirty black color, the assay should be discarded and a new determination made, using a fresh sample.[6]

$$\text{Weight of button} = \text{per cent metal in sample.}$$

$$\frac{\text{Weight of metal} \times \text{per cent Sn}}{.100} = \text{per cent Sn in the sample.}$$

NOTE.—This process should be carried on under a hood in a segregated room, and every precaution should be taken to avoid breathing the poisonous fumes of potassium cyanide.

THE SODIUM CARBONATE METHOD

The sample is fused with equal parts of sodium carbonate and sulfur.[7] The fusion is then dissolved in water. The tin goes into solution as a thiostannate of sodium. Iron and copper are then separated by the addition of sodium sulfite, leaving arsenic, antimony and tin in solution.[8]

[5] Lunge advises that the cyanide should not be allowed to boil. He uses a small sample (10 grams). "Technical Methods of Chemical Analysis," 1, Part 1, p. 256. It is our experience that satisfactory results are not obtained unless the extreme heat of the furnace is used.

[6] See also Mellor, "A Treatise on Chemical Analysis."

[7] Very finely divided carbon is sometimes preferred. Air must not be allowed to enter the crucible. Else decomposition is not complete. Mellor, "A Treatise on Chemical Analysis," p. 270 (1913). If carbon is used instead of sulfur the process becomes one of reduction to the metal and is carried out in the assay furnace. The details of operation are similar to the cyanide process. The metal separates as a button in the bottom of the crucible. The button contains other metals with the tin and must be analyzed further for exact percentages.

[8] Mellor objects to the method as being tedious and dirty.

OTHER METHODS OF OPENING TIN ORES

Fusion with Sodium Hydrate.—The sample of ore is fused with ten times its weight of sodium hydroxide. The process is carried out in a 60-ml. iron crucible, first fusing the NaOH and then adding the powdered mineral. A nickel crucible may be used, adding a little powdered charcoal to the NaOH before fusing. The fused mass is dissolved in water and the tin determined in the usual way,[9] after acidification with HCl.

Reduction by Means of Hydrogen.—The ore may be reduced by strongly igniting in a porcelain tube in a current of hydrogen. The reduced metal is then dissolved in hydrochloric acid and the tin estimated by a standard method.

Fusion with Sodium Peroxide.—J. Darroch and C. Meiklejohn[10] opened ores, slags, etc., by fusing with sodium peroxide in a nickel crucible. They dissolve the fused mass in hot water and acidify with hydrochloric acid. The sample is then ready for the necessary separations.

SEPARATIONS

Tin is separated from iron, aluminum, chromium, etc., by the insolubility of its sulfide in dilute hydrochloric acid. Tin, together with antimony, arsenic, platinum and gold, is separated from lead, mercury, copper, cadmium and bismuth, by the solubility of its sulfide in yellow ammonium sulfide. Antimony, arsenic, platinum and gold are precipitated as metals from a hydrochloric acid solution by the action of metallic iron, leaving tin in solution.

A few special separations are of interest.

Tin and Lead.—For the analysis of an alloy of lead and tin, it is usually preferable to make the estimations on different samples. In this case, lead is estimated by Thompson's method and the tin by Baker's modification of the iodine method. Lead can also be separated from tin by H_2S passed into an alkaline solution of NH_4OH. Lead may be separated as $PbSO_4$, no occlusion of tin occurs.

Tin and Copper.—This alloy can be dissolved in concentrated hydrochloric acid by the addition of potassium chlorate. A large excess of ammonium tartrate is added and the solution made alkaline with ammonia. Copper is then precipitated as sulfide by the addition of hydrogen sulfide water until no more precipitate is formed.

Tin and Antimony.—Antimony is separated, in the metallic form, from the hydrochloric acid solution of the alloy, by the action of metallic iron placed in the solution. The tin may be determined by the iodine method without the removal of the antimony. If the antimony is desired, it may be filtered off and determined in the usual way.

[9] Low, "Technical Methods of Ore Analysis," 3d Ed., pp. 208–213 (1908).
[10] Eng. Mining J., 81, 1177 (1906).

As in the case of lead, it is usually quicker and more accurate to make these determinations on separate samples. J. Silberstein (Chemist-Analyst, **19**, 14, 1930) recommends precipitation of copper by addition of red phosphorus and filtering.

Tin and Phosphorus.—One-half gram of the alloy is dissolved in 15 ml. of concentrated hydrochloric acid containing potassium chlorate. This is diluted to 200 ml. with water and warmed. It is then treated for a long time with hydrogen sulfide gas. The tin is all precipitated as sulfide while the phosphorus remains in solution.

Tin and Iron and Aluminum.—Tin is separated from iron and aluminum by precipitation, as sulfide, from the hydrochloric acid solution (2.4 ml. HCl per 100 ml.).

Iron may also be separated from tin with copper, and lead by precipitation as sulfide from the alkaline ammonium tartrate solution.

Tin and Tungstic Acid.—Donath and Mullner[11] separate tin oxide from tungstic acid by mixing the sample with zinc dust and strongly igniting in a covered crucible for fifteen minutes—boiling with dilute hydrochloric acid; oxidizing with potassium chlorate to change the blue tungstic oxide to tungstic acid and diluting with water. It is then allowed to stand overnight and filtered. The tin is in solution.

Tin and Silicon.—Dehydrate the silica by addition of H_2SO_4 and evaporation. Dissolve the tin sulfate. No loss of tin occurs.

Tin, Copper and Nickel.—Precipitate the tin, in presence of ammonium salts, by addition of NH_4OH according to the gravimetric method described on page 959.

Tin from Ag, Pb, Cu, Sb^{III}, As^{III}, Hg.—Copper, lead, silver or mercury may be deposited electrolytically from a solution containing nitric and hydrofluoric acids (5 ml. of each per 100 ml.). The tin may be recovered by evaporating the filtrate in platinum to remove H_2F_2, or by adding boric acid to bind the fluoride; the stannic tin may then be precipitated by H_2S, by cupferron or electrolytically, working in glass of Bakelite vessels.[12] In general the other metallic ions of the silver and copper-tin groups may be separated from stannic tin in sulfuric-hydrofluoric acid solution (5 ml. of each acid) per 100 ml. by hydrogen sulfide (sodium acetate may be added after most of the precipitation has occurred in order to reduce the acidity sufficiently to cause antimony and cadmium to precipitate). Arsenic and antimony are precipitated completely only if present in the trivalent state. Attack of materials by sulfuric acid and sulfur causes antimony and arsenic to remain trivalent, whereas tin goes readily to the quadrivalent state when the solution is diluted and treated with H_2F_2.

[11] J. Chem. Soc. Absts., **54**, 531, 1888.

[12] McCay, J. Am. Chem. Soc., 31, 373 (1909); **32**, 1241 (1910); **45**, 1187 (1923); McCay and Furman, ibid., **38**, 640 (1915); Furman, ibid., **40**, 895 (1918); Kling and Lassieur, Compt. rend., **170**, 1112 (1920); **173**, 1081 (1921); Furman, J. Ind. Eng. Chem., **15**, 1071 (1923).

GRAVIMETRIC METHODS FOR THE DETERMINATION OF TIN

DETERMINATION OF TIN OR THE OXIDES OF TIN BY HYDROLYSIS

This method depends upon the precipitation of meta-stannic acid in the presence of ammonium nitrate when the stannic chloride is diluted to considerable volume and heated to boiling. It is especially applicable to the determination of tin oxide in tin paste, but may be extended to all chloride solutions of the higher oxides. The reaction involved proceeds as follows:

$$SnCl_4+4NH_4NO_3+3H_2O=H_2SnO_3+4NH_4Cl+4HNO_3.^{13}$$

Stannous tin may be determined by oxidizing the chloride solution to the stannic form. The method gives concordant results and is rapid.

Procedure.—For the analysis of tin paste take a catch weight of about 10 grams for a sample. Dissolve this sample by heating it in a No. 6 beaker with 300 ml. of concentrated hydrochloric acid. Transfer the acid solution to a 500-ml. volumetric flask and make up to the mark with dilute (1 : 1) hydrochloric acid.

Take 50 ml. (approximately 1 gram) for a working sample. (If the determination is to be made on tin paste, the sample may be obtained directly by one of the methods described under Opening Tin Ores.) Dilute to 100 ml. with cold water. Nearly neutralize with concentrated ammonia and finish by adding drop by drop from a burette, dilute ammonia until a slight permanent precipitate is formed. A large amount of ammonia will tend to precipitate iron as $Fe(OH)_3$ if present, and to re-dissolve the meta-stannic acid.[14] Add 50 ml. of a saturated solution of ammonium nitrate. Dilute to 400 ml. with boiling water, stirring constantly. Bring the solution to boiling, remove from the flame and allow the beaker to stand on the steam bath until the precipitate has settled.[15] The solution above the precipitate should be clear. Decant the supernatant liquor through an ashless filter paper and wash the precipitate by decantation [16] six times, using 200 ml. of boiling water containing 6 g. NH_4NO_3 and allowing the precipitate to settle thoroughly at each washing. Transfer the precipitate to the filter, clean out the beaker and wash down with hot water in the usual way. After the precipitate has been allowed to drain, transfer to a porcelain or a silica crucible and dry carefully on an asbestos board over a Bunsen flame. When dry, ignite at a low temperature until the

[13] Fresenius, "Quantitative Chemical Analysis," 1, 406, 1903. Sodium sulfate may be used instead of ammonium nitrate. In that case the reaction is

$$SnCl_4+4Na_2SO_4+3H_2O=H_2SnO_3+4NaCl+4NaHSO_4.$$

[14] Some practice is required to judge accurately the exact point when the necessary amount of ammonia has been added. The precipitate should appear white.

[15] If the boiling continues more than a few seconds the precipitate will not settle properly. Time will be saved in this case if the sample is discarded and a new determination commenced.

[16] If meta-stannic acid is washed over onto the filter at this point, clogging will result and a great deal of time will be lost.

filter paper has been consumed.[17] Increase the heat and finally blast to constant weight.[18]

$$\frac{\text{Weight } SnO_2 \times 100 \times .7877}{\text{Weight of sample}} = \text{per cent Sn.}$$

NOTE 1.—If present in the solution the following would contaminate the SnO_2 oxides of Si, Cb, Ta, W, Sb, As, P(Fe Cu and Zu).

SEPARATION OF SnO_2 FROM OTHER METALLIC OXIDES[19]

Stannic oxide which is contaminated with ferric and cupric oxides, such as is obtained when copper-tin alloys are treated with nitric acid may be weighed. After treatment with ammonium iodide, the tin is volatilized in the form of SnI_4. The residual iodides may be converted back to the oxides (Fe_2O_3, and CuO) and weighed.

Procedure.—Ignite the separated metastannic acid to constant weight in a porcelain crucible. Then add to the impure tin oxide about fifteen times its weight of powdered ammonium iodide, and mix the two in the crucible intimately by means of a small spatula. Place the charged crucible in an electric crucible or muffle furnace maintained between 425° and 475° C. Allow it to remain there until all fumes have ceased to come from the crucible, about 15 minutes. Then remove the crucible and, after having allowed it to cool sufficiently, add 2 to 3 ml. of concentrated nitric acid. Evaporate to dryness on the hot plate and cautiously decompose the residual nitrates over a low burner flame. Follow this by ignition at low red heat to constant weight. The difference between this weight and the original weight gives the amount of pure stannic oxide present. A suitable correction should be applied if there is a weighable amount of nonvolatile matter in the ammonium iodide. To continue the analysis, dissolve the oxide residue out of the crucible by digestion with a few milliliters of hot concentrated hydrochloric acid. Dilute the resulting solution and filter it to remove small amounts of silica that may come from the filter paper ash. Finally add the solution and washings to the filtrate being evaporated down for the determination of lead as sulfate. The remainder of the analysis is conducted in the usual way.

PRECIPITATION OF TIN AS SULFIDE

The determination of tin as a sulfide involves many difficulties and should be avoided if possible. Better results can be obtained by the volumetric methods and in most cases without the necessity of preliminary separations of other elements. If tin must be separated as a sulfide, better results would be obtained if the precipitate were dissolved and the tin content determined by the iodine method.

Having the hydrochloric acid solution of tin after the interfering elements have been separated, to precipitate tin sulfide, neutralize with ammonia and then acidify with acetic acid. Pass hydrogen sulfide until the solution is saturated. Allow the precipitate to settle overnight. Pour the supernatant liquor off through a Gooch crucible and wash the precipitate six times by

[17] Spattering is likely to occur here, causing loss.

[18] If care is not exercized in this ignition some metallic tin due to carbon reduction will be obtained.

[19] E. R. Caley and M. G. Burford, Ind. Eng. Chem., Anal. Ed. 8, 114 (1936).

decantation, using a solution of ammonium nitrate [20] for wash water. Finally transfer to the crucible and wash free from chlorides. Dry the crucible in an oven at 100° C. Heat slowly in a Bunsen flame until [21] all the sulfur has been expelled. Care should be taken at this point to avoid forming fumes of stannic sulfide by heating too rapidly. Remove the lid of the crucible, which should be kept in place during the first part of the heating, and raise the temperature gradually, finally finishing with the blast. As sulfuric acid is usually present in some quantity, the crucible should be cooled and a small piece of ammonium carbonate should be placed in it. Repeat the ignition to drive out the acid. Cool and weigh as SnO_2.[22]

NOTES.—Tin may be separated from a number of elements by reduction with Zn, or Al or Cd in dilute HCl solution and then precipitate tin as metastannic acid by addition of NH_4OH.

Stannic chloride may be volatilized from a sulfuric acid solution by heating to 200° C. and passing HCl gas through the solution.

PRECIPITATION BY CUPFERRON; WEIGHING AS THE OXIDE [23]

This reagent is chiefly useful for the recovery of tin from the filtrate after separating it from other metals in solution containing 3–5% of concentrated H_2F_2. The filtrate is warmed with 4 g. boric acid to convert the fluoride to fluoborate. After cooling, preferably to 5 to 15° C., add an excess of 10% cupferron solution slowly with thorough stirring. The precipitate tends to become brittle after 20–30 minutes, and may then be filtered and washed very speedily with cold water. The precipitate is then dried and ignited very carefully and slowly until it is converted to SnO_2, in which form it is weighed after strong ignition.

The reagent separates stannic ion from Al, Cr, Mn, Zn, Ni, Co, and from moderate quantities of As and Sb provided they are in the form of arsenate and antimonate, which can readily be provided for by boiling the nearly neutral solution containing fluoride with ammonium persulfate. The solution should contain 5–10 ml. of free mineral acid per 200–500 ml. during the precipitation with cupferron.

[20] Sulfide of tin separates as a slimy mass which tenaciously retains alkaline salts, especially in the absence of ammonium salts. Mellor, "Treatise on Chemical Analysis," p. 308 (1913).

[21] Bichloride of tin, Acker process.

[22] This method is generally used only when minute traces of tin are present, and then it is considered best to dissolve the sulfide in hydrochloric acid and make the final determination by the iodine method. (See analysis of Canned Foods for "Salts of Tin," p. 971.)

[23] Kling and Lassieur, Compt. rend., 170, 1112 (1920); Furman, J. Ind. Eng. Chem., 15, 1071 (1923); Pinkus and Claessens, Bull. Soc. Chim. Belg., 31, 413 (1927).

BICHLORIDE OF TIN

Bichloride of tin is of great importance in some of the industries, especially the textile. It is necessary to have exact analytical control of the processes in which this compound is used in order to insure uniform results and to certify the efficiency and economy of the process. Several methods have been developed for this purpose. The ones given below have had practical application and have proven to be satisfactory.

STANNIC ACID METHOD.—HOT-WATER PRECIPITATION

In the textile industry where bichloride of tin is used, the efficiency of the process depends directly on the neutrality of the tin liquor. If there is more than enough chlorine present in the bichloride solution to exactly oxidize all the tin to the stannic form, this excess is called "free HCl." If there is not enough chlorine present to do this, the deficiency is spoken of as "basic HCl." The difficulty of determining the "free" or "basic" HCl is apparent when it is known that $SnCl_4$ readily decomposes in water, liberating free acid. The following method has been developed especially for this purpose and has given good results.

The important point in this analysis is to determine whether the liquor has "free" HCl present or whether it is "basic" in nature. It has been found that hot water precipitates tin from the $SnCl_4$ solution as stannic hydroxide and at the same time liberates the chlorine as free HCl.

$$SnCl_4+4H_2O=Sn(OH)_4+4HCl.$$ [24]

The $Sn(OH)_4$ separates in a colloidal precipitate which may be filtered off and the tin estimated as SnO_2. The liberated acid may be determined in the filtrate, and from this data the "free" or "basic" HCl can be calculated.

Procedure.—For accurate work about 20 grams of the liquor should be weighed out in a tared weighing bottle, but for works control, where time is an important factor, it is sufficiently accurate to get the specific gravity of the liquor by means of a hydrometer and take a measured quantity for a sample, calculating the weight from these data.

Transfer the sample to a 100-ml. volumetric flask. Make up to volume with cold distilled water. Draw out of this solution 10 ml. (approximately 2 grams) and place in a 150-ml. tall beaker. Fill the beaker nearly full with boiling hot water, stirring continuously while the water is being poured in.[25] Place the beaker on top of the steam bath and allow the precipitate to settle. Decant the liquor through an 11 cm. 590 S. & S. filter [26] and wash the precipitate six times by decantation, using hot water. Now transfer the precipitate to the filter and continue the washing until 1 drop of the filtrate gives no test for chlorine. After most of the water has drained out of the filter, place the

[24] Holleman and Cooper, "Text Book of Inorganic Chemistry," 4th Ed., 1912.

[25] If the solution is not stirred at this point, the precipitate will not settle and trouble will be experienced during the filtering process.

[26] Time may be saved by using a platinum cone with the filter and applying a gentle vacuum. This can be done with very little danger of breaking the paper.

paper and precipitate in a tared silica crucible. If there is plenty of time, dry the contents of the crucible on an asbestos board over a low Bunsen flame. In case the analysis must be made in a hurry, cover the crucible [27] and heat it very carefully over a low flame until all the water has been driven out and the paper has been charred. Then remove the cover and increase the heat to the full Bunsen flame and finally blast to constant weight. Weigh as SnO_2. Titrate the filtrate with N/1 NaOH, using methyl orange as the indicator.

Calculation:

$$SnO_2 \times .7877 = Sn$$
$$Sn \times 2.1949 = SnCl_4$$
$$SnCl_4 - Sn = Cl \text{ equiv. to } Sn$$
$$Cl \times 1.0285 = HCl \text{ equiv. to } Sn$$
$$\frac{HCl}{\text{Weight of sample}} = \text{per cent HCl equiv. to Sn}$$
$$\frac{\text{ml. N/1 NaOH} \times .03646}{\text{Weight of sample}} = \text{per cent HCl (actual).}$$

The difference between these last two figures equals "free" or "basic" HCl.

THE ACKER PROCESS METHOD

The theory of this method is practically the same as that of the hot-water method, except that in this case the liberated acid is neutralized with ammonia before the stannic hydroxide has been filtered off, the advantage being that any solution of the stannic hydroxide, by either acid or alkali, is prevented. The method is not applicable for the determination of "free" or "basic" HCl.

Procedure.—Weigh out 25 ml. of the bichloride of tin solution. Transfer to a 500-ml. flask (volumetric) and make up to volume with cold water. With a standardized pipette, transfer 25 ml. of this solution to a No. 4 beaker. Dilute with hot water to precipitate most of the tin as stannic hydrate. Add 10 drops of phenolacetolin (1 gram of phenolacetolin dissolved in 200 ml. of water). Titrate very carefully with dilute ammonia until the appearance of a rose-red color. Boil a few minutes on the hot plate. Allow the tin precipitate to settle. Decant through an 11-cm. filter paper. Wash rapidly with hot water without allowing the precipitate to cake down in the filter until the washings are free from chlorine. Dry the precipitate in an oven at 100° C. When dry, invert the filter into a tared porcelain crucible and heat on a gauze until the paper has disappeared. Remove the gauze and heat with the full Bunsen flame for a few minutes. Finally blast to constant weight.[28] Weigh as SnO_2.

Take the filtrate and washings and dilute them to a volume of 1000 ml. Warm 500 ml. of this solution and saturate it with hydrogen sulfide. If any tin separates, filter and ignite in a tared porcelain crucible. Moisten with a

[27] This precaution must be taken, else there will be a loss by decrepitation.

[28] If the oxide of tin is contaminated it may be dissolved by adding water saturated with SO_2 and acidifying with dilute HCl. Heat in a covered beaker (to prevent loss of tin). See article by E. Stelling, J. Ind. Eng. Chem., 16, 346 (1924).

little nitric acid and heat very slowly to drive out the acid. Ignite to constant weight. Weigh as SnO_2. Add this result to the SnO_2 obtained above when calculating the final result.

VOLUMETRIC DETERMINATION OF TIN

Volumetric methods for the determination of tin are based upon the reducing power of stannous compounds. They vary according to the oxidizing agent used and the details of manipulation.

LENSSEN'S IODINE METHOD AS MODIFIED BY BAKER [29]

This method is a modification of Lenssen's Iodine Method for the determination of tin in alkaline solutions. It is especially applicable to the determination of "salts of tin" in canned foods and to the estimation of tin coating on tin plate, but is accurate, rapid and very satisfactory for alloys and general analysis.

The method is based on the action of iodine in the presence of stannous chloride in hydrochloric acid solution. The reaction involved is:

$$SnCl_2+I_2+2HCl=SnCl_4+2HI.$$

A. Jilek reduces tin by means of iron, filtering off precipitated Sb, Cu and excess of Fe, in an atmosphere of CO_2. The reduced tin solution is now titrated with standard iodine.

Iron, lead and antimony do not interfere with the reaction. Copper in small quantities does not interfere with the determination, but if it is present in large quantities as a salt, it is likely to produce low results. Determinations made by the writer [30] show that results are accurate when less than 10% of copper, as copper chloride, is present. Larger amounts gave consistently low results. The reason for this fact centers around the difficulty of reducing all the copper to the cuprous form. If any $CuCl_2$ is left in the solution, it reacts with the potassium iodide of the iodine solution, causing the precipitation of CuI and the liberation of free iodine.

$$CuCl_2+2KI=CuI+2KCl+I.$$

Copper present as the metal is not easily soluble or goes into solution in the reduced form and is not likely to disturb the determination.

[29] H. A. Baker, Eighth International Congress of Applied Chemistry.

[30] Mr. B. S. Clark. Sulfates must not be present. They tend to have an oxidizing effect and spoil the results. There should always be an excess of bicarbonate of soda present in order that carbon dioxide will be generated during the washing process, thus preventing air from entering the flask at any time during the analysis.

Solutions—***Standard Tin Solution.***—Dissolve 5.79 grams of Kahlbaum's C. P. tin in C. P. hydrochloric acid. The solution of the tin is effected by placing about 150 ml. HCl in an Erlenmeyer flask, together with the tin, and boiling. After the tin has all been dissolved, transfer to a volumetric liter flask and make up to the mark with dilute hydrochloric acid.

$$1 \text{ ml.} = .00579 \text{ gram Sn.}$$

Standard Iodine Solution.—Dissolve 12.7 grams of C. P. iodine in a water solution of 20 grams of potassium iodide. Make up to one liter and standardize against the standard tin solution. For tin plate analysis, it is convenient to adjust the iodine solution so that 1 ml. equals exactly .00579 gram of tin. Then, if a sample of the plate having a total surface of 8 sq. ins. is taken, 1 ml. of the iodine solution is the equivalent of one-tenth of a pound per base box.

Indicator.—Dissolve 5 grams of pure soluble starch in 1 liter of water.

Air-free Water.—Dissolve 12 grams of bicarbonate of soda in 1 liter of water. Add 20 ml. HCl and allow the resulting gas to escape. Keep in a stoppered bottle.

Procedure.—For practical purposes, take a sample, such that the tin content will be between .2 gram and .5 gram.[31] A larger sample should be taken for extreme accuracy in order to decrease the possible technical error. Place the sample in flask *A* of the Sellars apparatus, Fig. 121, together with 100 ml. of concentrated C. P. HCl. Stopper the flask and connect tubes *B* and *D*, as shown in the illustration. Boil until the metal is all dissolved. This point is indicated by the cessation of the hydrogen evolution and the appearance of large well-developed bubbles. If a sufficient amount of metallic iron is present in the sample, complete reduction is assured. If no iron was present in the sample, or if there was not enough to reduce all of the tin, make sure that the tin is all converted to the stannous form by adding aluminum foil (about 1 gram). Replace the stopper and connect as originally. Boil until normal bubbles reappear. Open cock *C* to allow CO_2[32] gas to enter. Place the flask in cooling bath *F* without disconnecting the apparatus. After the solution has become thoroughly cool, disconnect tubes [33] and *D*[33] from the splash bulbs. Wash the bulbs with "air free" water, allowing the washings to drain into the bulk of the sample. Remove the stopper and wash down the sides of the flask. About 50 ml. of water should be used in the washing so that the final sample contains about 25% HCl. Add 5 ml. starch solution and titrate with the standard iodine solution.

$$\frac{\text{ml. iodine} \times .00579 \times 100}{\text{Weight of Sample}} = \% \text{ Sn},$$

or

$$\frac{\text{ml. iodine}}{10} = \text{pounds per " base box."}$$[34]

[31] According to experience at the Univ. of Southern California the amount of the sample should contain not more than 0.1 to 0.2 grams of tin.

[32] Carbon dioxide generated in a Kipp apparatus is likely to contain oxygen. It is much better to use liquid CO_2 such as can be purchased in the open market.

[33] See Fig. 121, page 969.

[34] "Basebox"—112 sheets of tin, 14×20 ins.

The Sellars Apparatus.—This apparatus is a device designed by Mr. W. S. Sellars for the purpose of facilitating the solution of tin samples out of contact with air. Added to this advantage, it is equipped with a water cooler. It is

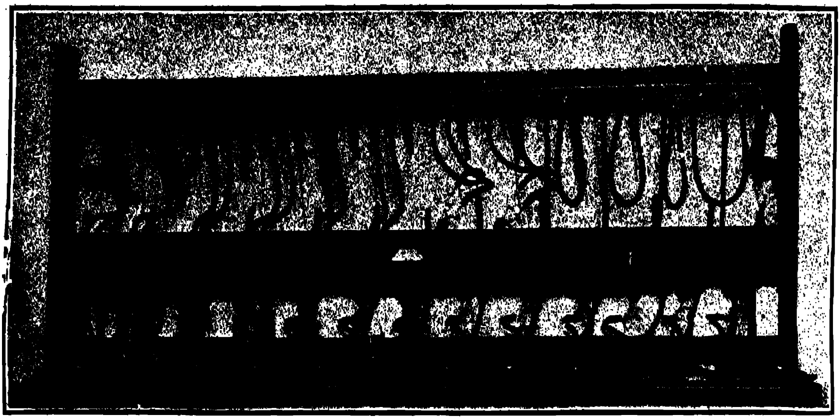


Fig. 119. Sellars' Apparatus.

also constructed so that the tubes and scrubbing bottles can be cleaned by flushing with water. The use of this apparatus practically eliminates the usual sources of error in connection with the iodine method, and at the same time greatly increases the speed of the determination. Fig. 120 shows the apparatus in operation.

A.[33] 300-ml. Erlenmeyer flask.
B.[33] Connection with reduced pressure line from liquid carbon dioxide cylinder.
C.[33] Glass manifold.
D.[33] Exit connection to trap.
E.[33] Water trap to prevent escape of HCl fumes and to prevent air from backing into the flask.
F.[33] Cooling tank.
G.[33] Low-pressure water wash-out manifold.
H.[33] Perforated feed pipe to water cooler.
K.[33] Outlet for cooler.
L.[33] Electric hot plate.
M.[33] Lead drain pipe.

FERRIC CHLORIDE METHOD[35]

This method depends upon the reduction of ferric chloride by stannous chloride in hot solution.

$$SnCl_2+2FeCl_3=SnCl_4+2FeCl_2.$$

[35] C. Mene, Dinglers Polytech. J., **117**, 230 (1850). K. Pallet and A. Allart, Bul. Soc. Chim. (2), 27, 43, 438 (1877). H. J. B. Rawlins, Chem. News, **107**, 53 (1913). H. Nelsmann, Z. Anal. Chem., **16**, 50 (1877).

Antimony, copper, arsenic, bismuth, mercuric chloride, tungsten and titanium must be absent.[36]

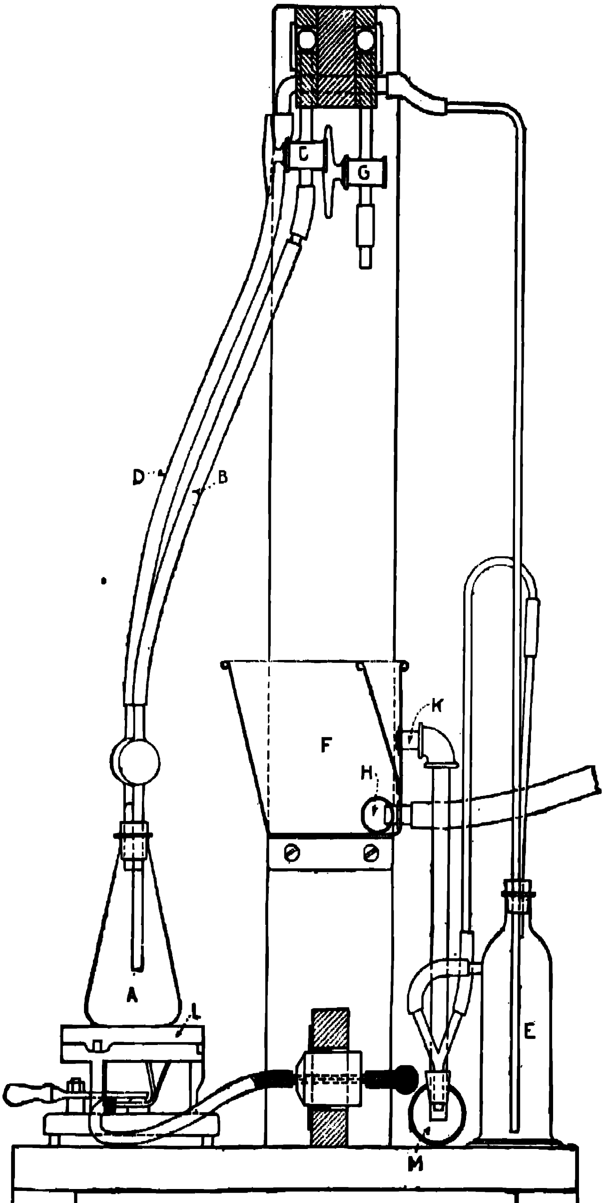


FIG. 120. Sellars' Apparatus. Diagrammatic Sketch.

The Standard Solution of Ferric Chloride is made by dissolving pure iron wire in hydrochloric acid. To standardize this solution, dissolve 1 gram of

[36] Lunge, "Technical Methods of Chemical Analysis," 2, Part I, p. 267.

pure tin in 200 ml. of C. P. HCl, preventing air from coming in contact with the solution by means of a trap, or by passing carbon dioxide over it.[37] Titrate this standard sample with the ferric chloride solution. The end-point is indicated by the yellow color, due to a slight excess of the iron solution.

Procedure.—Tin is first separated from the interfering metals in the usual way. If lead, copper, arsenic, antimony or bismuth are present, the sample is first reduced, in the hydrochloric solution, with iron wire. The solution is then filtered. Lead and tin remain in the filtrate. Neutralize by adding strips of zinc until the action ceases. Tin and lead are precipitated. The clear liquid should show no trace of tin with hydrogen sulfide. Allow the precipitate to settle and wash by decantation, keeping the precipitated metals in the flask. Add 150 ml. of concentrated hydrochloric acid, keeping the contents of the flask protected from the air, and bring to a boil. When everything is dissolved, titrate to a yellow color with the ferric chloride solution.[38] This part of the analysis should be done very quickly to prevent oxidation by the oxygen of the air.

RAPID VOLUMETRIC TIN DETERMINATION IN GENUINE BABBITTS[39]

The volumetric tin determination with iodine is not accurate in presence of copper exceeding 3%. High grade genuine babbitts often contain from 5 to 8% copper and the copper has therefore to be removed previous to the tin determination. This is most rapidly and conveniently accomplished by precipitating the copper with red phosphorus.

Vogel[40] in 1836 observed that yellow phosphorus precipitated copper from a solution of copper sulfate. This reaction takes place even if the solution contains as little as one gram molecule copper sulfate per 1,000,000 liters H_2O which corresponds to a sensitivity of .0000065% Cu.[41] Yellow phosphorus is however not as convenient to handle as the red, amorphous modification, which also can be used for precipitation of copper.[42]

To save time it is to be recommended to determine both tin and antimony in the same sample. After having dissolved the sample in sulfuric acid and determined the antimony by titration with permanganate the solution is transferred to a 400 ml. beaker, about a half teaspoonful red phosphorus added and the solution boiled for 15 minutes. The solution is then filtered through a Munktells filter No. 00 into a 500 ml. Erlenmeyer flask. Wash a few times with dilute H_2SO_4 (1 : 10) and discard the precipitate which contains the copper as copper phosphide. Add HCl and nickel strip to the solution, reduce and titrate the tin as usual with iodine using starch as indicator.

On precipitating the copper the phosphorus is oxidized to a state lower than orthophosphoric. This has, however, no influence on the subsequent tin determination.

[37] The Sellars apparatus can be used with advantage for this purpose.

[38] The end-point can be easily identified by looking at a blue Bunsen flame through the solution. When a small quantity of ferric chloride is present, the flame appears green. Mellor, "A Treatise on Chemical Analysis," p. 310 (1913).

[39] James Silberstein, Chicago, Ill., Chemist-Analyst, 19, 14 (1930).

[40] J. prakt. Chem., 8, 109 (1836).

[41] Z. anorg. allgem. Chem., 35, 460 (1903).

[42] J. Am. Chem. Soc., 42, 883 (1920).

VOLUMETRIC METHOD FOR TIN IN ALLOYS

The titration of stannous solutions by iodine may be represented by the following reaction:

$$SnO+2I+H_2O=SnO_2+2HI.$$

Sn is equivalent to O or to 2H, hence a normal solution contains one-half the molecular weight of Sn, or 59.35 grams per liter of solution.

Apparatus.—This consists of a 300-ml. Erlenmeyer flask, with a one-hole stopper, through which passes a quarter-inch glass tube, connected with a rubber tube 12 to 15 inches in length, the other end of the rubber tubing is connected with 2–3 inches of glass tubing, which dips in the beaker containing a bicarbonate of sodium solution.

Reagents.—0.1N iodine solution. Standardize against pure tin, using the procedure below. One ml. 0.1N I = 0.005935 g. of Sn.

Starch solution. Sulfuric and hydrochloric acids. Antimony, or iron, powder or test lead.

Procedure. ***Decomposition of the Sample.***—Tin alloys generally decompose in hydrochloric acid, but more readily in concentrated, hot sulfuric acid.

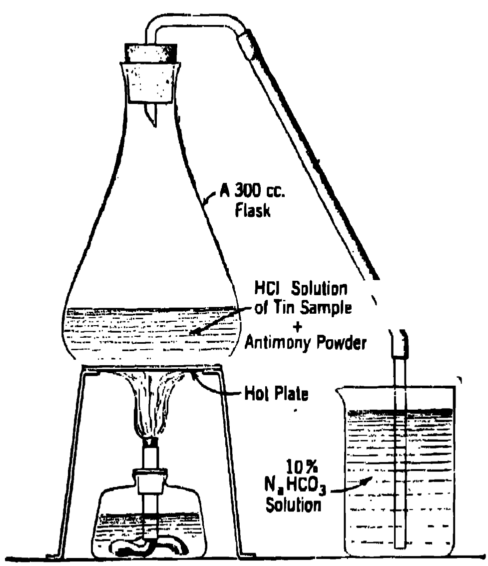


FIG. 121. Apparatus for Determination of Tin.

A sample containing, preferably, 0.1 g. Sn or less, is placed in a 300-ml. Erlenmeyer flask and 10 ml. of concentrated sulfuric acid added. The mixture is heated, preferably over a free flame, until the alloy completely disintegrates. Nearly all of the excess of free acid is expelled, keeping the flask in motion over the flame to lessen the tendency towards bumping, which is apt to occur during the concentration. The moist residue is allowed to cool.

One hundred ml. of (air-free) water are added followed by 50 ml. of concentrated hydrochloric acid and the mixture gently warmed until the solution

begins to clear. The apparatus is now assembled as shown in the figure, about 15 ml. of 10% (saturated solution) sodium bicarbonate being placed in the test tube (or 50 ml. in the beaker, if this is preferred to a test tube).

About 1 gram of very finely powdered reducing metal is placed in the flask, followed by 10 ml. of saturated sodium bicarbonate solution, the stopper being removed during the addition and then immediately replaced. The air is displaced by the CO_2 generated.[43]

The apparatus is now placed on a hot plate, or on an inverted sand-bath dish over a flame, and the solution is gently boiled for 10 to 15 minutes. The antimony should be of such fineness as to remain suspended during the ebullition of the liquid at this stage.

The beaker is now nearly filled with saturated sodium bicarbonate and the apparatus removed to a desk for a few minutes, and then placed in a cold water-bath of running water or under tap water, until the solution cools down to near room temperature. During this cooling carbonate will be sucked back into the flask " A " to establish pressure equilibrium, CO_2 being generated in the flask. Sufficient solution will remain in the test tube to act as a seal and prevent admission of air, which would spoil results by its oxidation of the tin.

The tubes are disconnected and 5 ml. of starch solution added by means of a pipette passing through the hole in the stopper (which should be loosened in the throat of the flask).

Standard iodine solution is now added, the tip of the burette passing through the hole of the stopper, agitating the solution by a " swirling " motion of the flask. The end-point is a blue color, which does not fade on stirring the solution.

If a factor weight has been taken, each ml. of the iodine of 0.1N strength is equivalent to 1 per cent of tin.

NOTES.—In the presence of copper a separation must be effected as over 3% copper interferes in this volumetric method especially when the percentage of the tin is low. High copper alloys do not decomposed readily in hydrochloric or sulfuric acids, but easily in dilute nitric acid. The solution obtained is evaporated to dryness, the residue is taken up with concentrated nitric acid, the oxide of tin (and antimony) remains insoluble, hot water is added and the solution filtered (hot) and the oxide washed once or twice with hot water. The tin (and antimony) is now best dissolved[44] by digesting for 3–5 minutes with 50 ml. of water saturated with SO_2 (at 60–70° C.), then 10 ml. of strong HCl are added to the solution heated to boiling and the SO_2 expelled by boiling. The solution is now ready for reduction with antimony by the method outlined above.

Tin may be reduced by iron, nickel or lead. If much copper is present this should be removed.

NOTE.—If iron is used for the reduction of tin HNO_3, W, Mo and V should be absent from the solution. W is reduced and colors the solution blue masking the end-point. Mo causes a brown coloration and will titrate causing high results for tin. V produces

[43] The method is capable of giving very excellent results from the experience of W. W. Scott and from that of advanced students in analytical chemistry and compares very favorably with the more elaborate procedure of passing CO_2 through the apparatus during the reduction and cooling. In the latter method, which we have commonly used, a Kipp generator proves to be very satisfactory. The CO_2 is scrubbed by passing through a solution of $NaHCO_3$ before entering the reduction flask. This procedure, although more cumbersome, has some advantage over the method described above, by having a constant atmosphere of CO_2 in the flask.

[44] Earnest Stelling, J. Ind. and Eng. Chem., 16, 346 (1924).

a purple color and also is titrated. If test lead is used for reduction the above do not interfere. The following do not interfere: SO_4, PO_4, I, Br, F, Fe, Ni, Co, Zn, Mn, Cl, Al, Cr, Pb, Bi, Sb, Mg, Ca, Ba, Sr, Mg.

ESTIMATION OF TIN IN CANNED FOOD PRODUCTS [45]

The tin in the canned food products is obtained as a sulfide precipitate from wet combustion, with nitric and sulfuric acids, of 100 grams food product.

The clear sulfuric acid residue is diluted, neutralized with ammonia and then rendered about 2% acid with hydrochloric acid, after which it is thoroughly saturated with hydrogen sulfide gas. This precipitate is then filtered on a Gooch crucible with a false bottom. The precipitate may contain foreign substances, such as lime, phosphorus, and silica, some lead, or even small amounts of iron, but none of these will cause any trouble subsequently in the titration, so that the labor of separating the tin completely from the precipitate is obviated.

After washing the precipitate three or four times in a Gooch crucible, it is transferred to a small porcelain dish by simply forcing out the false bottom of the Gooch crucible and its asbestos pad and rinsing off the crucible.

The precipitate, mixed with asbestos, is now transferred to a 300-ml. Erlenmeyer flask and boiled with concentrated hydrochloric acid, potassium chlorate being added from time to time to insure the complete breaking up and solution of the tin sulfide, as well as the elimination of the sulfur. This is accomplished in a very few minutes. A few strips of pure aluminum foil, free from tin, are then added to the flask until all of the chlorine is eliminated. The flask is then attached to the Sellars apparatus and the determination completed, according to the details given under the Iodine Method, using N/100 iodine solution.

Gravimetric Method.[46]—The sample is first digested to a colorless or pale yellow solution as described under Baker's method.

Add 200 ml. water to the digested solution and pour into a 600-ml. beaker. Rinse out the Kjeldahl flask with three portions of boiling water so that the total volume of the solution is about 400 ml. Allow to cool and add 100 ml. concentrated ammonia. This amount of ammonia should render the solution nearly neutral, unless more than 50 ml. sulfuric acid have been used for digestion. The solution should be tested to see that it is still somewhat acid. In case of a large excess acid, add ammonia until just alkaline and then make about 2% acid with hydrochloric or sulfuric acid. Pass in a slow stream of hydrogen sulfide for an hour, having the covered beakers on an electric hot plate at about 95° temperature. Allow to digest on the hot plate for an hour or two.

[45] H. A. Baker, Eighth International Congress of Applied Chemistry.
[46] E. L. P. Treuthardt, Association of Official Agricultural Chemists, August 15, 1915.

Filter the tin sulfide on an 11-cm. filter. Wash with three portions of wash solution alternated with three portions of hot water. The wash solution is made up of 100 ml. saturated ammonium acetate, 50 ml. glacial acetic acid, and 850 ml. water.

Place the filter and precipitate in a 50-ml. beaker and digest with three successive portions of ammonium polysulfide, bringing to a boil each time and filtering through a 9-cm. filter. Wash with hot water. Acidify with acetic acid, digest on the hot plate for an hour and filter through a double 11-cm. filter. Wash with two portions of wash solution alternated with hot water and dry thoroughly in a weighed porcelain crucible. Thorough drying is essential to the success of the determination. Ignite very gently at first and later at full heat of Bunsen flame. Finally heat strongly with large burner, or Méker burner, having the crucible partly covered. Stannic sulfide must be gently roasted to the oxide, but the oxide may be heated strongly without loss, due to volatilization.

Weigh the stannic acid and convert to metallic tin by the factor .7877.

OTHER INDUSTRIAL METHODS FOR DETERMINATION OF TIN

FUSION METHOD [47]

Solution Required. *Standard N/10 Iodine Solution.*—Prepare a solution of iodine as described in "Determination of Tin in a White Metal Alloy." Standardize by weighing out 0.3 g. of pure tin filings, brush into a 300-ml. cone flask, add 20 ml. H_2SO_4 (sp.gr. = 1.84) and heat on a hot place, until dissolved. Cool and dilute with 50 ml. of water. In the meantime, fuse 20 g. of Na_2O_2 in an iron crucible, leach out with least amount of water; carefully transfer to the flask containing the tin, add 70 ml. HCl (sp.gr. = 1.18), dilute to a volume of 250 ml., add 4 pieces of iron and heat over a low flame until nearly dissolved.[48] Introduce four more pieces of iron, insert a rubber stopper carrying a delivery and reduce as before. Proceed as described in "Determination of Tin in a White Metal Alloy."

Method.—Weigh out 0.5–1.0 g. of the finely ground sample, brush into an iron crucible of 60-ml. capacity in which has been placed 10 g. Na_2O_2, mix, cover with 10 g. Na_2O_2, place lid loosely on crucible and heat over a good sized Bunsen flame. As soon as the melt is in quiet fusion, hold the crucible with a pair of tongs, impart a twirling motion and fuse for two minutes longer. Allow the melt to cool on the sides of the crucible by slow twirling as the mass solidifies. When cold, set the crucible on its side in a 400-ml. beaker, cover with a clock glass, add 100 ml. of water and leach. Remove lid and crucible, washing with least amount of water, add 120 ml. HCl (sp.gr. = 1.18); transfer to a 500-ml. cone flask, add iron wire and reduce over a low flame. When the iron is nearly all dissolved and the solution shows no tinge of yellow, filter

[47] By courtesy of the National Lead Company.

[48] The time required to nearly dissolve the iron should be about 40 minutes and the solution should show no tinge of yellow. If a yellow color persists, add two pieces of iron and continue the reduction.

through glass wool into another 500-ml. cone flask in which has been placed iron wire. Wash flask 3 times and glass wool 3 times with hot distilled water. The volume of solution should now be about 250 ml. Insert a rubber stopper carrying a bent delivery tube and continue the reduction. Proceed as described in the "Determination of Tin in a White Metal Alloy."

Run a blank by fusing 0.1 g. powdered antimony with Na_2O_2 and proceed as described in the "Determination of Tin."

Make correction for blank and calculate to per cent of tin present. Duplicate titrations should not disagree more than 0.1 ml.

DETERMINATION OF TIN IN A WHITE METAL ALLOY

The National Lead Company uses the following procedure.

Apparatus.—A delivery tube made of glass tubing 5 mm. in inside diameter is bent into an inverted letter, the small end of which is fitted in a No. 6 rubber stopper. When the stopper is inserted in the mouth of the flask, the short end of the tube should just pass through the stopper and the other end should reach to a level 1 in. from the bottom of the flask and be 1 in. distant from the flask.

Solutions Required. ***Sodium Bicarbonate Solution.***—Place 10 g. of $NaHCO_3$ in a 100 ml. beaker and fill with cold distilled water.

Starch Solution.—To 1000 ml. of boiling water add a cold suspension of 6 g. of starch in 100 ml. of distilled water; cool, add a few drops of oil of cassia, mix and reserve for use.

Standard N/10 Iodine Solution.—Weigh out 12.7 g. of pure sublimed iodine and 18 g. of potassium iodide, transfer to a 500-ml. beaker, add about 35 ml. of cold distilled water and allow to digest in the cold for several days. Dilute to nearly 700 ml. with distilled water and filter through glass wool into a 1000-ml. graduated flask. Do not wash. Make up to the mark and mix thoroughly. Standardize by weighing out 0.3 g. of pure tin filings and 0.1 g. of powdered metallic antimony into a 300 ml.-cone flask. Add 20 ml. H_2SO_4 and proceed exactly as described in the determination for the analysis of the alloy.

METHOD A

(a) The sample contains less than 0.03 g. of copper.

Determination of Tin.—Weigh out from 0.5 to 2 g. of the sawings,[49] brush into a 300 ml. cone flask, add 20 ml. H_2SO_4 (sp.gr. 1.84) and heat on a bare hot plate [50] until completely decomposed. Cool, add 100 ml. of cold distilled water and 20 ml. HCl (sp.gr. 1.18), introduce four pieces of iron [51] and heat on an asbestos covered hot plate over a low flame until the iron is almost but not entirely dissolved. A reduction of 40 minutes duration is sufficient to completely reduce the tin. Filter off the precipitated metals through glass wool into a 500 ml. cone flask in which has been placed four pieces of iron, washing the flask three times and the funnel three times with hot distilled water. The volume at this point should be about 250 ml. Fit the delivery tube in the mouth of the flask, set over a low flame and reduce as before. When the reduction is complete, set the bicarbonate solution so that the free end of the delivery tube is immersed in it. When gas bubbles start to pass through the $NaHCO_3$ solution, remove both flask and beaker from the stove, allow to cool at room temperature for about 10 minutes and then cool [52] the flask in running water. When cold, remove the delivery tube, withdraw any undissolved iron with a magnetic file, washing both removed iron and file with cold dis-

[49] Pass a hand magnet through the sample before weighing.

[50] Too high a heat will cause the solution to spit.

[51] The iron for reducing the tin is the ordinary strap iron used for strapping shipping cases. Each piece should be 2 in. long and ½ in. wide, weigh about 2 g. and be free from grease, lacquer and rust.

[52] Keep the delivery tube in the mouth of the flask and the free end immersed in the $NaHCO_3$ solution during the whole cooling operation.

tilled water, add 2 ml. of starch solution and titrate with the standard iodine solution to the first permanent tinge of blue.

Run a blank by treating 0.1 g. of powdered metallic antimony exactly as the metal itself was treated.

Make correction for the blank and calculate for tin content.

Accuracy.—Duplicate titrations should not disagree more than 0.1 ml.

METHOD B

(*b*) The sample contains more than 0.03 of copper.

Weigh out from 0.5 to 2 g. of the sawings, brush into a 250-ml. beaker, add 15 ml. HNO_3 (1 : 1) and heat until completely decomposed. Evaporate to near dryness, add 5 ml. HNO_3 (sp.gr. 1.42), dilute to a volume of 150 ml., bring to boiling and allow to stand in a warm place one hour. Filter on a 9 cm. paper to which has been added a little pulp [53] and wash two or three times with hot dilute HNO_3 (1 : 50). Transfer the paper and precipitate to a 300 ml. cone flask, add 20 ml. H_2SO_4 (sp.gr. 1.84) and 5 g. of $K_2S_2O_7$ and heat over a flame until the paper has been completely decomposed and the clear solution is perfectly colorless. Cool, add 100 ml. of water, 20 ml. HCl (sp.gr. 1.18), four pieces of iron and proceed as in Method (*A*).

The Editor acknowledges assistance in the preparation of this chapter by the following: B. S. Clark, American Can Company; W. J. Brown, National Lead Company. Other names appear throughout the chapter.

[53] Paper pulp may be prepared by tearing several 11 cm. of Whatman No. 40 filters into small pieces, introduce them into a 300 ml. cone flask, add 100 ml. of hot distilled water, stopper and shake vigorously until pulped.

TITANIUM

(Ti, *at.wt.* 47.90; *sp.gr.* 4.5[1]; *m.p.* 1795° C. (±15°)[2]; *oxides* TiO, Ti_2O_3, TiO_2, TiO_3)

Titanium[3] is an abundant element, occurring only in the combined state in nature. It is found in igneous, metamorphic and sedimentary rocks, especially in basic silicate rocks. The element is widely distributed in minerals, soils, clays and titaniferous iron ores. It is found in granite, gneiss, mica, slate, syenitic rocks, granular limestone, dolomite, quartz, feldspars and a large number of other minerals. The principal minerals are:

Ilmenite, $FeTiO_3$, containing 35–60% TiO_2.
Rutile, TiO_2, containing 90 to 100% TiO_2.
Titanite, $CaTiSiO_5$, containing 34 to 42% TiO_2.
Perovskite, $CaTiO_3$, containing about 60% TiO_2.

N.B.—List by W. M. Thornton, Jr., A. C. S. Monograph Series, No. 83, p. 23.

Titanium dioxide is now extensively used as a white pigment in protective coatings, paper, rubber, rayon, etc. It is commercially produced in the pure form and as composite pigments such as titanium-barium pigment (25% and 30% TiO_2, 75% and 70% $BaSO_4$) and titanium-calcium pigment (30% TiO_2, 70% $CaSO_4$), and also as a lead titanate ($PbTiO_3$). The white titanium pigments are characterized by their exceptional tinting strength and hiding power, excelling in this respect any other commercial white pigments.

Another important application of titanium is the use of ferrotitanium in the iron and steel industry. The function of the titanium is to remove oxygen and nitrogen from steel and consequently to yield a product free from blowholes and at the same time prevent segregation to a great extent, especially of carbon, phosphorus and sulfur. In a steel thus purified the natural strength and resistant properties of the material are developed in the highest degree. Titanium is also used in small amount in the 18–8 stainless steels to prevent intergranular carbide precipitation thereby improving the corrosion resistance.

Titanium has also found application in the textile and leather industries. In the dyeing of leather, titanium potassium oxalate has been found particularly well adapted. The use of titanous chloride and titanous sulfate for bleaching or discharging colors is increasing. Such bleaching agents are particularly applicable for silk and wool, which are injured by the action of those bleaching agents in which chlorine is the active element.

[1] M. A. Hunter, Eighth Int. Congress Applied Chem. 2, 127 (1912).

[2] G. K. Burgess and R. G. Waltenburg, Bull. Bur. Standards 10, 88 (1914), Scientific paper No. 205.

[3] Titanium was discovered in the mineral ilmenite by Gregor (1789) and later found in rutile and named titanium by Klaproth (1793). The element is used in removing oxygen and nitrogen in steel. Its use is increasing.

Titanium compounds are also used for electric light filaments, arc-light electrodes, ceramics, fine brown glazes, paint for iron and steel, coating of welding rods, etc.

DETECTION

The powdered ore is fused with potassium pyrosulfate until effervescence ceases. The cooled mass is dissolved in 10% sulfuric acid by boiling. **Hydrogen peroxide,** H_2O_2, added to this titanium solution, produces a yellow to orange color, according to the amount of titanium present. Hydrofluoric acid, or fluoride, destroys the color. Vanadium also produces this color with hydrogen peroxide, but the color is not destroyed by HF. The reaction is often assumed to be due to the formation of pertitanic acid, H_4TiO_5, but is more apt to be from an ion like $[TiO_2(SO_4)_2]^{=}$.[4] Uranium, molybdenum and chromate also give colors with hydrogen peroxide.

Morphine produces a crimson color with solutions of titanium in sulfuric acid. (N.B.—Thymol color reaction—Lenher and Crawford, J. Am. Chem. Soc. 35, 138, 1913.)

Zinc added to hydrochloric acid solutions of titanium produces a violet color,[5] tin a fine violet solution.[6] A green color results if fluorides are present.

Sulfur dioxide, SO_2, passed into a solution of titanium containing iron reduces the latter and permits the precipitation of white hydrous titanium oxide by boiling a slightly acid solution.

Bead Test on Charcoal.—A small portion of the powdered mineral heated on charcoal with microcosmic salt and tin produces a violet-colored bead if titanium is present. A platinum wire loop may be used in the reducing flame.

ESTIMATION

Both gravimetric and volumetric methods are used in the determination of titanium. In recent years the gravimetric method has given place to the accurate, rapid and less involved volumetric and colorimetric procedures.

In the usual analytical procedures a part of the titanium may remain with the silica residue, from which it must be recovered. The remainder precipi-

[4] R. Schwartz, Z. anorg. allgem. Chem. 210, 303 (1933).
[5] M. H. Sainte-Claire Deville, Chem. News 4, 241 (1861).
[6] E. Cahen and W. O. Wootton, "The Mineralogy of the Rarer Elements," London, Charles Griffin Co., 1920, p. 127.

tates upon addition of NH_4OH with iron, aluminum, etc., and unless accounted for will lead to an error in iron and aluminum determinations. If the reduction of iron is made by use of zinc, the error will fall largely on iron, as titanium is also reduced by zinc; if SO_2 or H_2S are used for reducing iron the error will fall largely on aluminum, as titanium is not affected by these reagents.

Titanium ores are readily attacked by hydrofluoric acid; the acid, however, must be removed completely by repeated evaporation with sulfuric acid, otherwise it interferes with the colorimetric determination of titanium by means of peroxide, since it bleaches the color. In titanium solutions a moderate amount (10–20%) of acid must be present to prevent precipitation of titanium by hydrolysis.

In dissolving titanium precipitates from filter paper loss is apt to result by incomplete solution, small amounts remaining on the filter and escaping attention.

PREPARATION AND SOLUTION OF THE SAMPLE

A knowledge of the solubility of the element and its oxides is of value in dissolving the sample.

Element.—This is freely soluble in cold dilute hydrochloric or sulfuric acids; more readily so when the acids are heated. It is soluble in cold, concentrated hydrochloric acid; readily soluble in hot, concentrated hydrochloric or sulfuric acids. It is scarcely acted upon by nitric acid, but readily dissolved in hydrofluoric acid. The dissolving of titanium in hydrofluoric acid, however, is accompanied by a loss of material—due perhaps to the evaporation of titanium fluoride.[7] It is soluble by fusion in acid potassium sulfate.

Oxides.—Ti_2O_3, which has a black or blue color, is soluble in concentrated hydrochloric or sulfuric acids, forming, in the latter case, a violet-colored solution.[8] The oxide is insoluble in water and in ammonium hydroxide.

TiO_2 is difficultly soluble in concentrated sulfuric acid, less soluble if strongly ignited. The hydrous titanium oxide, precipitated at elevated temperatures, requires concentrated hydrochloric or sulfuric acid to effect solution; when precipitated at room temperature (by addition of alkali) it is readily soluble in cold, dilute acids. TiO_2 is soluble in acids upon fusing with alkalies; it is also soluble in hydrofluoric acid, forming TiF_4, which is volatile, unless an excess of sulfuric acid is present (distinction from silica). The ignited oxide is best dissolved by fusion with $KHSO_4$ and heating the fused mass with dilute sulfuric acid solution.

Artificially prepared ignited titanium dioxide dissolves readily in a mixture of concentrated sulfuric acid and ammonium sulfate on boiling.

Titanium dioxide, on being fused with an alkali, gives a titanate. If this be treated with water, an acid titanate is formed, which remains almost entirely undissolved. This residual material, however, may be dissolved with the aid of concentrated mineral acid.

Salts.—Many titanium salts are decomposed through the agency of water, hydrous titanium oxide being precipitated; the extent of the hydrolysis de-

[7] M. A. Hunter, J. Am. Chem. Soc. 32, 335 (1910).
[8] M. Ebelmen, Ann. Chim. (3), 20, 392 (1847).

pends upon the quantity of water added, the temperature, and other conditions. Titanium sulfate is soluble in water, if care is taken to add water to the salt gradually and in small increments; concentrated solutions are reasonably stable, although titanyl sulfate, $TiOSO_4 \cdot 2H_2O$, may crystallize out on standing; dilute solutions gradually hydrolyze. Some of the double salts are readily soluble and their solutions stable, e.g., potassium titanium oxalate.

Solution of Steel.—The sample may be dissolved in hydrochloric acid (1 : 2). If a residue remains, it is treated with a mixture of equal parts of hydrofluoric and sulfuric acids and a few drops of nitric acid, in a platinum dish, and the mixture evaporated to sulfuric anhydride fumes and to complete expulsion of hydrofluoric acid. The colorimetric procedure is now used for estimating titanium.[9]

NOTE.—Titanium in steel treated with ferro carbon-titanium exists in two conditions: (1) Titanium soluble in hydrochloric acid. (2) Titanium insoluble in hydrochloric acid. Of the very small amount of titanium in treated steel the greater part will usually be found in the second form. When the amount of titanium in the steel is exceedingly small, the soluble titanium frequently exceeds the insoluble, and it is then occasionally desirable to determine also that existing in the second form.

Alloys.—These are dissolved in concentrated nitric acid, aqua regia or a mixture of the dilute acids. Should nitric acid be used, the excess is expelled by evaporation to dryness with hydrochloric acid. The metals of the hydrogen sulfide group are removed in an acid solution by precipitation with H_2S, and titanium determined colorimetrically in the filtrate.

Ores.—One to 5 grams of the ore are treated with 10 to 50 ml. of a mixture of sulfuric and hydrofluoric acids (1 : 5), a few drops HNO_3 added, and the solution evaporated to fumes to expel HF. If a residue remains upon taking up with water containing a little sulfuric acid, it is filtered off and fused with $KHSO_4$ as directed under the fusion method.

Fusion Method for Ores.—The finely powdered sample is fused with four to five times its weight of potassium bisulfate, $KHSO_4$, and the cooled fusion dissolved with dilute sulfuric or hydrochloric acid. In the presence of silica potassium fluoride is added to assist in the decomposition of the material.

Fusion with sodium carbonate or sodium pyrosulfate are frequently recommended. G. W. Sears and L. Quill have found [10] that in the decomposition of rutile it is advisable to use 12.5 parts of pyrosulfate to 1 part of the mineral and in case of titanite the proportion must be increased to 35 : 1. The titanium is leached out with water or dilute acid. Most of the silica, and if present, the tantalum and columbium, remain in the insoluble residue. Some alkali silicate goes into solution, and must be removed in gravimetric determinations.

(See Analysis of Titaniferous Ores, page 995.)

Titaniferous Slags.—One-half gram of the finely ground sample is decomposed in a platinum dish by a mixture of 5 ml. water, 5 ml. concentrated sulfuric acid, 2 ml. nitric acid, and 10 ml. of hydrofluoric acid, the reagents being added in the order named. The solution is evaporated rapidly to SO_3 fumes to expel fluorides and the excess sulfuric acid until residue is left nearly dry.

[9] See also O. L. Barnebey and R. M. Isham's work (J. Am. Chem. Soc. 32, 957 (1910)) on the colorimetric determination of titanium in hydrochloric acid solution.

[10] G. W. Sears and L. Quill, J. Am. Chem. Soc. 47, 929 (1925).

After cooling it is taken up with 40 ml. of dilute hydrochloric acid (1 : 3), which will give a clear solution containing all the constituents of the slag except silica, which has been volatilized as SiF_4. The solution is diluted to 200 ml. with cold water. Iron and titanium are precipitated by ammonia in slight excess and filtered at once without boiling. The precipitate is dissolved in cold dilute hydrochloric acid and reprecipitated with ammonia. Titanium is now separated from iron by reducing iron with SO_2 and precipitating titanium from a boiling acid solution, as described on page 981.

SEPARATIONS

Less interferences occur in the volumetric and colorimetric methods so that these are generally preferred to the gravimetric procedures. Occasions may demand one or more of the methods of separation given below.

Separation of Titanium from the Hydrogen Sulfide Group Elements.—Hg, Pb, Cu, Cd, As, Sb, Sn, Rh, Pd, Os, Ru, Au, Pt, Ir, Mo, Te, Se.—The members of the hydrogen sulfide group with a solution acidity of 1.5 ml. H_2SO_4 or 2.4 ml. HCl [11] per 40 ml. are precipitated if the solution is saturated with H_2S and diluted to 100 ml. and again saturated with H_2S. The addition of 1 gram of tartaric acid per 0.2 gram of oxides present is recommended, specially if a further separation from certain members of the ammonium sulfide group is to be made. The sulfides are filtered off and washed, titanium passing into the filtrate.

Separation of Titanium from Iron, Cobalt, Nickel, Zinc (and the greater portion of manganese).—The filtrate from the above separation is taken and 0.5–1 g. ammonium bisulfite added (to assist in complete precipitation of Ni and Co), ammonium hydroxide added in slight excess and the solution again saturated with H_2S. Titanium (Be, Cb, Cr, Ta and Zr) remains in solution, while Fe, Co, Ni, Zn (and a large portion of Mn) precipitate as sulfides. The solution is filtered and titanium determined in the filtrate.

NOTES.—It is advisable to dissolve the precipitate and reprecipitate the sulfides to recover minute amounts of occluded Ti.

Tartaric acid (also salicylic acid) in the solution containing titanium is removed by evaporating to fumes with H_2SO_4 and adding HNO_3 and again evaporating. (See gravimetric method following.)

OTHER METHODS

Separation from Copper, Zinc, Aluminum, Iron, etc.—Titanium is precipitated from a slightly acid solution [12] by boiling, passing sulfur dioxide through the solution to keep the iron reduced and prevent its precipitation.

[11] A. A. Noyes and W. C. Bray, Tech. Quarterly 19, 235 (1906).
[12] Acidity exactly 0.5% is best according to L. Levy, Chem. News 56, 206 (1887).

Separation from the Bivalent Metals, Manganese, Nickel, Cobalt, Zinc.—Titanium is precipitated along with aluminum and iron by hydrolysis of its acetate in a hot, dilute solution, whereas manganese, nickel, cobalt and zinc remain in solution.

A sharp separation of titanium from manganese can be effected with ammonium hydroxide alone.[13]

Separation of Titanium from Aluminum.—Cupferron Method.—By this procedure large amounts of aluminum may be separated from small amounts of titanium. (One part of Ti and 28 parts of Al.) The reverse does not appear to be true. Cupferron (nitroso-phenylhydroxylamine) is added to the decidedly acid solution containing titanium and aluminum, a flocculent titanium salt precipitating and aluminum remaining in solution. A 6% water solution of the reagent is added until a fine precipitate appears (after complete precipitation of the curdy titanium precipitate), which redissolves in an excess of the reagent.[14]

The titanium precipitate is washed by decantation and then on the filter with very dilute hydrochloric acid to remove traces of aluminum. The procedure affords a separation of titanium from chromium, nickel, cobalt, manganese. Copper, iron, zirconium, vanadium, tungsten, and uranium (UO_2) precipitate with the titanium, if present in the solution.

NOTE.—Cupferron precipitates titanium (as well as zirconium, thorium, etc.) notwithstanding the presence of tartaric, citric, and other organic acids containing hydroxyl groups. See also under "Separations" in chapter on Zirconium.

Separation of Titanium from the Alkaline Earths, etc.—The hydroxide is precipitated when a titanium solution containing ammonium chloride is treated with ammonium sulfide, whereas barium, strontium, calcium and magnesium remain in solution. Titanium hydroxide may be precipitated by making the solution containing titanium slightly ammoniacal with NH_4OH.

Separation of Titanium from Iron—Ether Extraction of Iron.—Details of this procedure are given in the chapter on Iron under Separations. Iron must be in ferric form (trivalent) as divalent iron is not extracted. The chloride solution containing free HCl is repeatedly extracted with ether in a separatory funnel. All but 1–2 mg. of ferric iron passes into the ether layer. The ether also extracts trivalent gallium,[15] quantitatively, quinquivalent Sb, hexavalent Mo, trivalent Tl, trivalent Au, considerable trivalent As, while the following remain in solution—Al, Bi, Ca, Cd, Cu, Fe (divalent), Pb, Mn, Ni, Se, V, Ti, U, Zn, Zr, members of the platinum group, rare earths, W (with PO_4). (See table by Swift—reference 15.)[16]

Separation of Titanium from Zirconium and Thorium.[17]—The nitric acid solution is carefully treated with a solution of sodium carbonate to neutralize the greater part of the free acid and to the boiling hot solution is slowly added

[13] G. E. F. Lundell and H. B. Knowles, J. Am. Chem. Soc. 45, 676 (1923).

[14] W. M. Thornton, Jr., Am. J. Sci. (4), 37, 407–14 (1914); W. M. Thornton, Jr., "Titanium" A.C.S. Monograph Series, No. 33, N. Y. Chem. Cat. Co. (1927), pp. 58, 90, 95, 96, 98, 107, 109–11, 115, 121, 126, 128, 163, 168, 170, 180, 184, 188, 191, 200, 213, 224; G. E. F. Lundell and H. B. Knowles, J. Ind. Eng. Chem. 12, 344 (1920).

[15] E. H. Swift, J. Am. Chem. Soc. 46, 2376 (1924).

[16] Cr^6, Al, Ga^3 also dissolve.

[17] M. Dittrich and S. Freund, Z. anorg. allgem. Chem. 56, 344 (1908).

a 20% solution of ammonium salicylate in sufficient excess to precipitate completely the zirconium (and thorium, if present). The mixture is boiled gently for about half an hour or more, diluted to about 200 ml. and filtered hot. The precipitate is washed with a hot, 20% solution of ammonium salicylate until its color is only faintly yellow or white. Titanium passes into the filtrate.

Separation of titanium, zirconium, etc. from chromium, vanadium, molybdenum, tungsten, phosphorus, and arsenic may be effected by fusing with sodium carbonate and a little sodium nitrate and thereafter extracting with water.[18]

Separation of Titanium from Molybdenum, Phosphorus, and Vanadium.—The separation is necessary when the colorimetric determination of titanium is to be made, since these elements interfere. The presence of ferric iron is necessary for complete precipitation of titanium. The separation is made by carefully neutralizing the greater part of the free acid present by addition of a solution of NaOH and pouring the mixture into 150 ml. of a hot, normal solution of NaOH, filtering and washing with hot dilute NaOH (0.5 N).[19] It is advisable to repeat the precipitation to remove traces of the interfering elements, the titanium being brought into solution with HNO_3 and H_2SO_4 or by fusing with $NaHSO_4$.

The separation of aluminum from titanium, tantalum, columbium, molybdenum, arsenic, fluorine, and boron with the aid of 8-hydroxyquinoline is of interest. Reference is made to the work of G. E. F. Lundell and H. B. Knowles: J. Research Nat. Bur. Standards **3**, 94 (1929) for details.

Separation from Tantalum and Columbium.—W. R. Schoeller and E. C. Deering, Analyst **52**, 625 (1927). See chapter on Columbium and Tantalum.

GRAVIMETRIC METHODS

GRAVIMETRIC DETERMINATION OF TITANIUM. MODIFIED GOOCH METHOD[20]

This method is applicable to minerals and metallurgical products that are comparatively high in titanium. The method provides for the separation of titanium from iron and from aluminum and phosphoric acid with which it commonly occurs. The procedure as proposed by F. A. Gooch and modified for non-aluminous rocks by Wm. M. Thornton, Jr., gives reliable results. The details of the method with a few slight changes found to be advantageous are given below. Iron is separated from titanium by precipitation as a sulfide in presence of tartaric acid, the organic acid is destroyed by oxidation and tita-

[18] See W. F. Hillebrand, U. S. Geol. Survey, Bull. 700, 185 (1919).

[19] Addition of a little Na_2SO_4 to the NaOH solution is recommended.

[20] F. A. Gooch, Proc. Am. Acad. Arts and Sci., New Series, **12**, 435 (1885); Wm. M. Thornton, Chem. News **107**, 121 (1913).

nium precipitated from a boiling acetic acid solution. In the presence of alumina and phosphoric acid, Gooch, in his original process,[21] fused the first precipitate of titanium oxide (after ignition) with sodium carbonate, treated the melt with boiling water, filtered, ignited the residue, fused again with a little sodium carbonate, dissolved the entire mass in sulfuric acid, and then precipitated the titanium again by hydrolysis of the acetate.[22] The removal of zirconium (see separations) is necessary.

Procedure. Preparation of the Sample. Ores High in Silica.—These may be decomposed by taking to SO_3 fumes with a mixture of 10 to 15 ml. of 50% hydrofluoric acid, HF, and 3 to 4 ml. of concentrated sulfuric acid per gram of sample.

Oxides.—Decomposed by fusion with sodium or potassium bisulfate. The fusion is dissolved in 10% sulfuric acid, keeping the volume as small as possible. The sample should contain not over 0.2 gram titanium.

Precipitation of Iron.—To the solution containing titanium, tartaric acid, equal to three times the weight of the oxides to be held in solution, is added. This should not exceed 1 gram of the organic acid, as the subsequent removal of larger amounts would be troublesome. H_2S is passed into the solution to reduce the iron and NH_4OH added to slight alkalinity followed by a further treatment with H_2S to completely precipitate FeS. The solution should be faintly alkaline (litmus). After filtration and washing of the ferrous sulfide with very dilute and colorless ammonium sulfide, the titanium is entirely in the iron-free filtrate.

Oxidation of Tartaric Acid.—The organic acid is oxidized by addition of 15 to 20 ml. of concentrated sulfuric acid to the sample placed in a 500-ml. Kjeldahl flask. The solution is evaporated to incipient charring of the tartaric acid. After cooling slightly, about 10 ml. of fuming nitric acid are added cautiously, a few drops at a time, and when the violent reaction has subsided the flask is heated gradually (hood), a vigorous reaction taking place accompanied by much effervescence and foaming with evolution of copious brown fumes. The organic matter gradually disappears, the effervescence becomes steady and finally ceases and white fumes of SO_3 are given off. The solution is cooled and the pale yellow syrup poured into 100 ml. of cold water, the flask washed out, adding the rinsings to the main solution. The solution is filtered, if necessary.

Precipitation.—Ammonia is added until the solution is nearly neutral (a point where the solution is slightly turbid, the precipitate dissolving upon vigorous stirring). If a trace of iron is suspected about 1 ml. of 10% ammonium bisulfite is added. Five ml. of glacial acetic acid followed by 15 grams of ammonium acetate or its equivalent in solution is added and the volume of the solution made up to about 350 ml. The solution is brought rapidly to boiling and maintained in ebullition for about three minutes. The titanium will precipitate in white flocculent and readily filterable condition. The precipitate is washed first with water containing acetic acid and finally with pure

[21] F. A. Gooch, Proc. Am. Acad. Arts Sci., New Series, 12, 444 (1885).

[22] All things being considered, the cupferron method is far superior to the acetate hydrolysis involving the destruction of the tartaric acid by sulfuric and nitric acids; even though the latter process yields reasonably accurate results; W. M. Thornton, Jr., Am. J. Sci. (4) 34, 214 (1912).

water. The filter and the precipitate are ignited cautiously at first over a low flame and finally over a Meker blast for twenty minutes. The residue is weighed as TiO_2.

In the presence of large amounts of alumina and phosphoric acid, the residue above obtained is fused with sodium carbonate in a platinum dish and the fusion leached by boiling with pure water. Alumina and phosphoric acid go into solution as soluble sodium salts and titanium oxide remains insoluble in the residue.

NOTES.—Titanium may be separated from aluminum by fusing the residue with potassium acid sulfate, $KHSO_4$, and precipitation of titanium in an acid solution by cupferron. Al_2O_3 is in solution.

The interfering action of rare earths should be kept in mind, also of members of the hydrogen sulfide group (these can be removed by an extra filtration in the course of separating the iron as ferrous sulfide), vanadium (especially quinquivalent), tungsten, and uranium (quadrivalent but not sexivalent).[23]

DETERMINATION OF TITANIUM IN FERRO CARBON TITANIUM

GRAVIMETRIC METHOD[24]

Into a 6-in. porcelain evaporating dish, weigh 0.6 gram (factor weight) of alloy.

Dissolve in a mixture of 15 ml. of dilute sulfuric acid (one vol. of acid to one of water), 5 ml. of nitric acid, and 10 ml. of hydrochloric acid. Evaporate to fumes of sulfuric anhydride.

Cool and take up by boiling with 50 to 60 ml. of water and 5 to 10 ml. hydrochloric acid. Filter into a 500-ml. beaker and wash the residue with hot water and dilute hydrochloric acid.

In the filtrate precipitate iron and titanium by ammonia in slight excess. Filter without boiling and wash precipitate twice on filter with hot water.

Reject filtrate. Dissolve the precipitate in a very little dilute hydrochloric acid, washing the filter with hot water and collecting the solution and washings in the original beaker.

Nearly neutralize the solution with ammonia or ammonium carbonate; dilute to 300 ml.; saturate with sulfur dioxide gas, and boil until hydrous titanium oxide is precipitated and the solution smells faintly of sulfur dioxide.

Filter and wash with hot water and dilute sulfurous acid.

Dry, ignite, and weigh as titanium dioxide.

Since the factor weight of sample has been used, one milligram of titanium dioxide is equal to 0.1% metallic titanium.

Cupferron may with advantage be applied to the estimation of titanium in either ferro-carbon-titanium or carbon-free ferro-titanium (W. M. Thornton, Jr., A. C. S. Monograph Series, No. 33, N. Y. Chem. Cat. Co. (1927), p. 200; T. R. Cunningham, Ind. Eng. Chem., Anal Ed. 5, 305 (1933)).

[23] See W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," p. 454 (1929). John Wiley & Sons, Inc.

[24] Methods of analysis used in the laboratories of the Titanium Alloy Manufacturing Company.

VOLUMETRIC METHODS

THE DETERMINATION OF TITANIUM BY REDUCTION, ADDITION OF FERRIC SALT AND TITRATION OF REDUCED IRON WITH POTASSIUM PERMANGANATE[25]

Principle.—Titanium in solution is reduced by means of zinc, an excess of ferric sulfate is added and the ferrous salt, formed by reduction by the titanous salt, is titrated with standard permanganate. The method is more accurate than direct titration of the titanous salt with permanganate.[26]

Preparation of the Sample

Procedure.—One to 2 grams of the ore is decomposed by hydrofluoric and sulfuric acids or by fusion with potassium pyrosulfate or a combination of the two according to the methods already described. Members of the H_2S group, if present, may be removed by H_2S. If iron is present it may be determined by boiling off the H_2S in the filtrate containing Fe, Ti, etc., and allowance made in the titration for titanium. If other interfering elements are present in this filtrate,[27] titanium oxide may be precipitated by boiling the slightly acid solution (sulfurous acid) according to directions given in the gravimetric method. The oxide may be brought into solution by fusion with pyrosulfate, dissolving the melt with dilute sulfuric acid.

Reduction.—The solution is washed into a 100-ml. flask and diluted with water so that it will contain 10% of sulfuric acid. This acid holds titanium oxide in solution. Sufficient zinc to cause complete reduction is added and a rubber stopper carrying a Bunsen valve tube and a thistle tube with glass stop-cock is inserted in the neck of the flask. The evolved hydrogen expels the air and reduces the titanic salt to the titanous form. Iron if present is also reduced. Gentle heat is applied until the excess of zinc dissolves. The solution is cooled and an excess of ferric sulfate added through the thistle tube, followed immediately by cold distilled water until the flask is filled to the neck. The contents of the flask is poured into a No. 6 beaker containing 150 to 200 ml. of cold distilled water and the ferrous iron, formed by the reducing action of titanous salt, is titrated with N/10 $KMnO_4$ solution.

One ml. N/10 $KMnO_4 = 0.00479$ gram Ti, or 0.00799 gram TiO_2.

THE DETERMINATION OF TITANIUM BY REDUCTION WITH ZINC IN A JONES REDUCTOR AND TITRATION WITH PERMANGANATE[28]

The reduction of titanium in a Jones reductor proceeds rapidly and is quantitative, provided the reduced solution is caught under a 3–5-fold excess of ferric sulfate.

[25] In Newton's method (H. D. Newton, Am. J. Sci. (4) **25**, 130–4 (1908)) a blank experiment must be made so as to be able to correct for any iron (or other reducing substance) that may be in the zinc.

[26] T. R. Ball and G. McP. Smith, J. Am. Chem. Soc. **36**, 1839, (1914).

[27] Organic matter, As, Sn, Sb, Cb, Cr, Fe, Mo, V, U, W interfere.

[28] G. E. F. Lundell and H. B. Knowles, J. Am. Chem. Soc. **45**, 2620 (1923). See also work by E. F. Hickson, Proc. A.S.T.M. **24**, I, 859 (1924).

The reduction is conveniently carried on in solutions containing 3–5% by volume of sulfuric acid and may be done at 25°–30°.

The determination is carried out as follows:

Using a Jones reductor of 19 mm. internal diameter, with zinc column 43 cm. in length, there is added in order 25–50 ml. dilute sulfuric acid, 3 to 5% by volume; 150 ml. of the titanium solution containing 3 to 5% by volume of sulfuric acid; 100 ml. more of acid and finally 100 ml. of water. The reduction is performed at a speed of about 100 ml. per minute.

The reduced solution is delivered through a tube from the reductor under and into a ferric sulfate solution containing about .02 g. of iron per ml. in 8% by volume sulfuric acid. The ferric sulfate solution should be from 3 to 5 times that theoretically required by the titanium. The reduced solution is titrated with tenth normal potassium permanganate.

VOLUMETRIC METHOD BY REDUCTION OF TITANIUM AND TITRATION WITH A FERRIC SALT

The following volumetric method recommended by the National Lead Company—Titanium Division, is essentially that described by P. W. & E. B. Shimer, Proceedings of Eighth International Congress of Applied Chemistry, the method hereafter described differing principally in the form of reductor and also in a few details of operation.

Reagents.—Standard ferric ammonium sulfate solution of which 1 ml. is equivalent to 0.005 grams of TiO_2, standardized by reduction and titration with 0.1 N potassium permanganate which has been standardized against Bureau of Standards sodium oxalate, Standard Sample No. 40b.

Dissolve 60 grams of the ferric ammonium sulfate in 600 ml. of distilled water acidified with 20 ml. of sulfuric acid. Add potassium permanganate solution drop by drop as long as the pink color disappears. Dilute the solution to two liters. In standardizing, 50 ml. of the solution is made up to about 100 ml. in 5% H_2SO_4 solution, reduced in the Jones Reductor and titrated against standard 0.1 N $KMnO_4$; or 0.2 gram c.p. TiO_2 (100%) is run by this same method.

Indicator.—Saturated solution of ammonium thiocyanate.

Reductor.—A dispensing burette about 22 inches long, 2 inches in diameter and equipped with a glass stop-cock and delivery tube 6 mm. wide $\times$ 3½ inches long. The reductor is charged with an 8 inch column of 20 mesh amalgamated zinc (1500 grams) and on top of this a 6 inch column of broken amalgamated stick zinc (about 750 grams). The delivery tube is connected to a one liter flask through a three-hole rubber stopper. One hole is used as an inlet and another as an outlet for carbon dioxide gas.

The zinc is amalgamated by immersing it in a solution of mercury bichloride in hydrochloric acid. Eleven grams of $HgCl_2$ is dissolved in 100 ml. of concentrated HCl. Two hundred fifty grams of zinc is covered with distilled water in a one liter suction flask and the $HgCl_2$ solution is poured in, slowly mixing and shaking for about two minutes. The solution is poured off, the zinc washed thoroughly with hot tap water and finally with distilled water.

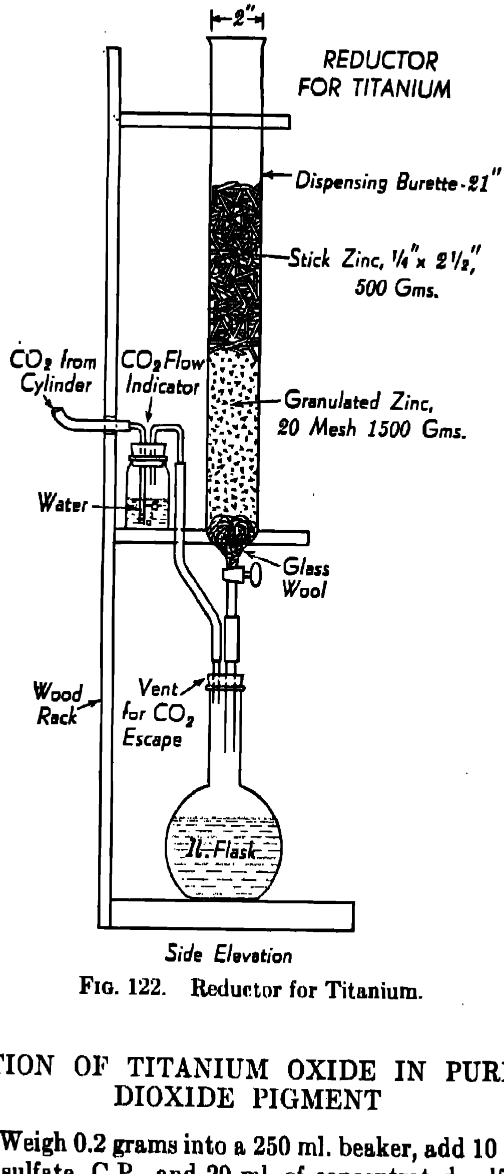


FIG. 122. Reductor for Titanium.

DETERMINATION OF TITANIUM OXIDE IN PURE TITANIUM DIOXIDE PIGMENT

Procedure.—Weigh 0.2 grams into a 250 ml. beaker, add 10 grams of ammonium or sodium sulfate, C.P., and 20 ml. of concentrated sulfuric acid; cover the beaker with a watch glass and digest to complete solution on the hot plate or Meker burner. (A Bunsen burner may cause bumping.)

If the pigment should prove refractory and offer resistance to solution in the above quantities of ammonium sulfate and sulfuric acid, these are varied until the material dissolves.

The titanium solution should not contain more than 0.25 gram TiO_2, should contain 10–15% H_2SO_4, and have a volume of 125–150 ml.

Drain the reductor to the top of the fine mesh zinc. Add 200 ml. of a hot, freshly boiled solution of H_2SO_4 (5%). Slowly drain the reductor; then wash

at least four times with hot freshly boiled water—tap water may be used. Drain the reductor to the top of the fine mesh zinc; wash the hot titanium solution into it and allow to remain from 15 to 20 minutes. During the whole period of reduction a slow stream of carbon dioxide is passed through the receiving flask. Slowly drain the reductor into the receiving flask while continuously passing carbon dioxide through the flask. When the solution has reached the level of the fine mesh zinc, add a hot freshly boiled 5% solution of sulfuric acid and bring the level of the solution to the top of the stick zinc. Drain to fine mesh zinc; then wash in the same manner four times with hot freshly boiled water. Tap water may be used but should be boiled long enough (about 20 minutes) to expel the dissolved oxygen. Remove the flask, add 7 ml. of the indicator and titrate rapidly with the standard ferric ammonium sulfate solution.

NOTES.—In titrating the titanium solution with ferric ammonium sulfate, greater accuracy is obtained by adding nearly all of the ferric ammonium sulfate before agitating; then agitate by shaking with a gentle rotary motion and continue until the final end point, which is a light straw color. Usually one-tenth of a ml. is deducted from the ferric ammonium sulfate reading for the blank.

DETERMINATION OF TITANIUM IN FERRO-CARBON TITANIUM

One-half gram of sample is dissolved in a 6-in. porcelain evaporating dish in a mixture of 10 ml. water, 10 ml. sulfuric acid, 5 ml. of hydrochloric acid, 5 ml. of nitric acid.

The solution is evaporated to fumes of sulfuric anhydride; taken up by boiling with 50 ml. water and 10 ml. of hydrochloric acid; filtered and washed with hot water and hydrochloric acid.

The filtrate and washings should be about 100 ml. in volume.

The reductor is prepared for use by first passing through it a little hot dilute sulfuric acid followed by hot water, finally leaving sufficient hot water in the reductor to fill to the upper level of the zinc.

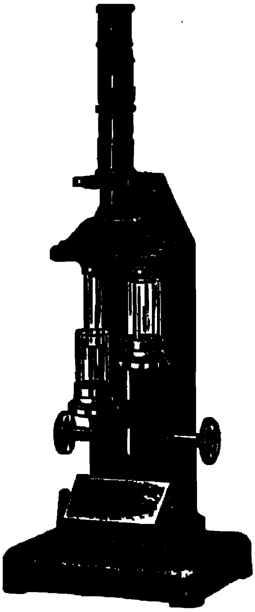
The hot titanic solution prepared as described above is now introduced into the reductor and the titanium content determined as above.

COLORIMETRIC DETERMINATION OF TITANIUM WITH HYDROGEN PEROXIDE

Preliminary Considerations.—Hydrogen peroxide added to acid solutions of titanium produces a yellow to orange color, the depth of the color depending upon the amount of titanium present. Upon this fact the method is based. It is of especial value in determining small amounts of titanium, as it is possible to detect less than one part of the metal per hundred thousand parts of solution. Color comparisons can best be made on samples containing 0.05 to 5 milligrams of the element; larger amounts produce too deep a color for accurate comparison.

The following interferences should be made note of, e.g., molybdenum, vanadium and chromium also produce a color that would lead to error. Iron if present to the extent of 4% or over produces a color that must be allowed for; e.g., 0.1 gram Fe_2O_3 in 100 ml. of solution is equivalent to about 0.2 gm. of TiO_2

oxidized by H_2O_2 in 100 ml. of solution. Fluorides destroy the color, hence must be absent.[29] Phosphoric acid and alkali sulfates have a slight fading action,[30] hence must be allowed for by adding equivalent amounts to the standard if they are present in the sample. The addition of an excess of sulfuric acid partly counteracts the action of phosphates or alkali sulfates.[31] The color intensity is increased by increase of temperature, hence the standard and the sample examined should have the same temperature.[32] Since hydrous titanium oxide produces only slight if any color with hydrogen peroxide, its formation must be prevented; the presence of 5% of free H_2SO_4 accomplishes this.[33]



By courtesy of Arthur H. Thomas Company, Philadelphia, Pa.

FIG. 123. Colorimeter.

DIRECTIONS FOR THE USE OF A DUBOSCQ TYPE OF COLORIMETER

The mirror is turned so that the two halves of the field appear to be equally illuminated with the cups clean and empty. The solutions are then poured into the cups. The cup containing the standard solution is then lowered to a definite thickness of the standard solution between the bottom of the cup and the end of the plunger. With this movement the half of the field corresponding to the standard solution is seen to darken, while the other half remains luminous and colorless. If the cup containing the unknown solution is now moved in its turn, the two halves of the field are brought to the same intensity, after which the height at which the two liquid columns display this equal absorptive power is read by means of this scale. The proportion of coloring matter in two solutions is inversely proportional to the heights of the two columns necessary to obtain the same intensity of illumination, thus if the standard tube is set at 10 mm., and the solution under examination is the same intensity of color at 20 mm., the latter is just one-half the concentration of the standard. This is usually expressed by the formula:

Color of test solution ÷ Color of standard solution = Height of standard solution ÷ Height of solution to be tested.

If, therefore, the scale reading is 20 mm. for the standard, and 15 mm. for the solution to be tested, the formula reads: $20/15 = 1.33$.

If, for example, the standard solution contains 4 ml. of coloring matter in 100 ml., the solution under test will be found to contain $4 \times 1.33 = 5.32$ ml. in 100 ml.

The procedure is very satisfactory for magnetic or other iron ores. It is fully as accurate as the best gravimetric method and very much more rapid. Experimental studies[34] have shown that it is possible to determine 0.007 mg. of TiO_2/100 ml. in a 50 ml. layer in the Duboscq colorimeter with an average

[29] W. F. Hillebrand, J. Am. Chem. Soc. 17, 718–19 (1895); Chem. News 72, 158 (1895).

[30] P. Faber, Z. anal. Chem. 46, 277 (1907).

[31] H. E. Merwin, Am. J. Sci. (4) 28, 121 (1909).

[32] W. F. Hillebrand, U. S. Geol. Survey, Bull. 700, p. 155 (1919).

[33] F. P. Dunnington, J. Am. Chem. Soc. 13, 210 (1891); Chem. News, 64, 302 (1891).

[34] H. Ginsberg, Z. anorg. allgem. Chem. 226, 57 (1935).

error of $\pm 10\%$. The various colorimetric methods for titanium with a good bibliography have been collected by the Snells.[35]

Solutions Required. Standard Titanium Solution.—This may be prepared by precipitation of TiO_2 from K_2TiF_6 according to the gravimetric procedure and purification by solution and reprecipitation, the fluorine being first removed by taking the compound to fumes with H_2SO_4 and then hydrolyzing titanium with NH_4OH. The washed precipitate is ignited over a Méker flame for fifteen minutes, cooled in a desiccator and placed in tightly stoppered bottle, since TiO_2 is slightly hygroscopic.[36] Pure titanium dioxide may be precipitated from titanium tetrachloride solution.[37]

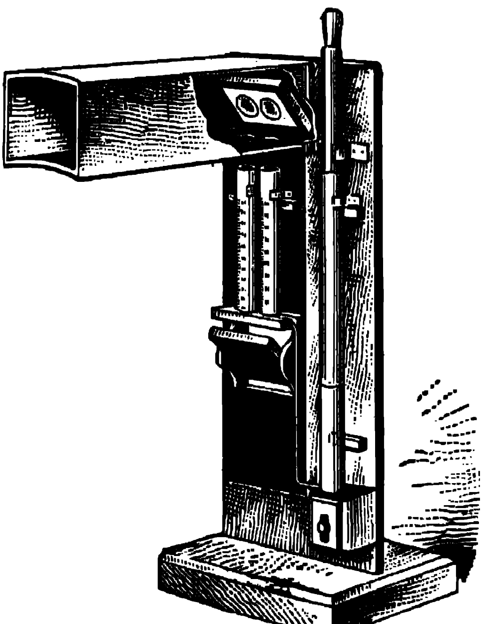


FIG. 124. Colorimeter.

Five-tenths gram of TiO_2 is fused with about twenty times its weight of $KHSO_4$ in a platinum dish, keeping at fusion heat until the oxide has dissolved. A high temperature is not advisable. The fusion is dissolved in 5% sulfuric acid by gently heating. The solution washed into a 500 ml. graduated flask is made up to volume with 5% H_2SO_4. One ml. contains 0.001 gram TiO_2, or 0.0006 gram Ti.

Preparation of the Reagent.—Potassium titanium oxalate [$K_2TiO(C_2O_4)_2 \cdot 2H_2O$], Baker's C.P. salt is recrystallized once from water, and the crystals dried at room temperature for several days. Enough of this material (about 4.5 grams) to contain 1 gram of titanium dioxide is mixed with 8 grams of

[35] F. D. Snell and C. T. Snell, Colorimetric Methods of Analysis, Van Nostrand, 1936.
[36] Thornton recommends potassium titanium oxalate as an initial substance from which to prepare a standard solution of titanic sulfate for use in colorimetric analysis; (see W. M. Thornton and R. Roseman, Am. J. Sci., (5) 20, 14 (1930)).
[37] W. W. Plechner and J. M. Jarmus, Ind. Eng. Chem., Anal. Ed. 6, 447 (1934).

ammonium sulfate, and this mixture placed in a 500-ml. Kjeldahl flask. One hundred ml. of concentrated sulfuric acid (sp.gr., 1.84) are added and heat applied gradually. At the beginning there is a slight foaming; but the liquid soon becomes calm. At length the solution is heated to boiling and maintained at that point for several minutes. The whole heating operation can be completed in 20 minutes, the solution being thereby freed from oxalic acid which, if present, might later bleach the peroxidized standard. The resulting solution is diluted with water to 800 ml., cooled, poured into a 1-liter volumetric flask, and diluted to the mark; whereupon it is filtered and stored in a glass-stoppered bottle. One may test for the complete destruction of oxalate by adding a drop of potassium permanganate to a portion of the filtered solution. There should be no decolorization of the permanganate.

Hydrogen Peroxide.—30% solution. If this is not available sodium peroxide dissolved in dilute sulfuric acid may be used.

Apparatus.—Colorimeter—Fig. 124. Also see Fig. 59, page 519.

Preparation of the Sample.[37a]—The solution of the sample having been obtained by one of the procedures given under Preparation and Solution of the Sample, the element may be determined according to the procedure given below. If interfering substances are present, e.g., comparatively large amounts of iron, or if tungsten, vanadium or chromium are present it will be necessary to precipitate titanic acid by adding ammonium hydroxide to the boiling solution as directed under the gravimetric determination of the element. The washed precipitate is dissolved in sulfuric acid.

Procedure.—The sulfuric acid solution of titanium should contain 5% of free sulfuric acid. It is poured from the beaker in which solution was effected into a 100-ml. Nessler tube, 2 ml. of hydrogen peroxide, 30% solution are added and the volume made up to 100 ml. with 5% sulfuric acid. The standard is prepared by pouring 40 to 50 ml. of 5% sulfuric acid into a second 100-ml. Nessler tube, adding 2 ml. of 30% hydrogen peroxide, H_2O_2, followed by sufficient standard titanium solution to exactly match the sample and the solution made up to 100 ml. with 5% sulfuric acid. The titanium solution is added from a burette, noting the exact volume required. From this the percentage of titanium in the sample can readily be calculated. If iron is present in the sample, an equivalent amount should be added to the standard. If a colorimeter is used, a standard should be prepared which is deeper in color than the sample examined. The standard is poured into the comparison cylinder and the two tubes compared. By raising or lowering the plunger (see illustration) the standard solution is forced in or drawn out of the comparison tube. When the colors match, the reading in the comparison tube will indicate the amount of TiO_2 present in the sample. The solution may be mixed by stirring with a platinum spiral.

Example.—One-gram sample required 20 ml. of titanium standard solution, 1 ml. of which contained 0.001 gram TiO_2. Then the sample contains

$$\frac{0.001 \times 20 \times 100}{1} = 2\% \ TiO_2.$$

If the colorimeter has been used and 150 ml. of standard made by adding 30 ml. of standard titanium solution and it is found that the column of liquid

[37a] M. L. Kilpatrick, O. M. Reiff, and F. O. Rice, J. Am. Chem. Soc. 48, 3019 (1926).

in the standard comparison tube stands at 85 ml., the calculation would be as follows: 150 ml. contains 30×0.001 gram TiO_2, therefore 85 ml. are equivalent to $\frac{85 \times 0.03}{150} = 0.017$ gram TiO_2 per gram or 1.7%.

For the practical application of the colorimetric method in determining titanium in steel the following procedure is given.

NOTE.—*Separation of Titanium from Iron.* J. H. Walton, Jr.,[38] separates titanium from iron by fusing the finely powdered substance with three or four times as much sodium peroxide, and extracts the fusion with water. The filtrate contains the sodium pertitanate whereas the iron oxide remains on the filter paper. The filtrate is acidified with H_2SO_4 until 5% of free acid is obtained and the color of this solution compared with a standard obtained by fusing a known weight of TiO_2 with Na_2O_2 and extracting and treating with H_2SO_4 as in case of the sample.

COLORIMETRIC DETERMINATION OF TITANIUM IN STEEL TREATED WITH FERRO-CARBON TITANIUM[39]

The titanium in steel treated with ferro-carbon titanium exists in two conditions:

(1) Titanium *insoluble* in hydrochloric acid.
(2) Titanium *soluble* in hydrochloric acid.

Of the very small amount of titanium in treated steel the greater part will usually be found in the first form, and ordinarily the determination of titanium in this form answers every purpose of identifying and judging the quality of titanium-treated steel.

When the amount of titanium in the steel is exceedingly small, the soluble titanium frequently exceeds the insoluble and it then is sometimes desirable to determine also that existing in the second form.

Reagents. ***Peroxide Solution.***—Dissolve 4 grams of sodium peroxide in 125 ml. dilute sulfuric acid (1 of acid to 3 of water), and dilute to 500 ml.

Concentrated Standard Titanium Solution. Stock Solution.—One-fourth gram of a standard 20% carbonless ferro-titanium[40] is dissolved in 30 ml. dilute sulfuric acid (1 acid to 3 water). When solution is complete it is oxidized by the least possible quantity of concentrated nitric acid, boiled for a few minutes, cooled and diluted to such a volume that 1 ml. will contain 0.0005 gram of titanium.

When using a 5-gram sample 1 ml. is therefore equal to 0.01% titanium.

Dilute Standard Titanium Solution.—This solution is made, just before making the determination, by diluting one volume of the concentrated standard titanium solution to ten volumes.

One ml. of this solution contains 0.00005 gram of titanium and is equal to 0.001% of titanium when using a 5-gram sample.

[38] J. H. Walton, J. Am. Chem. Soc. 29, 481 (1907).

[39] By L. E. Barton. Method of analysis recommended by the Titanium Alloy Manufacturing Company.

[40] Ferro-titanium suitable for the preparation of standard titanium solutions is made and supplied by the Titanium Alloy Manufacturing Company, Niagara Falls, N. Y.

Apparatus. ***Pipettes and Burettes.***—The pipettes for measuring the concentrated standard solution and burette for delivering the dilute standard solution should be carefully calibrated.

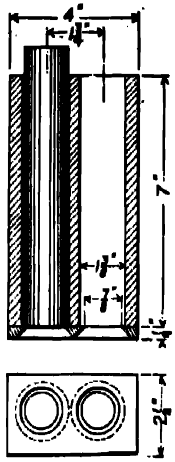


Fig. 125. Colorimeter Block.

Nessler Jars.—These should be graduated with 50-ml. mark. It is convenient to have a set of four.

Colorimeter.[41]—The colorimeter or comparator consists of a rectangular block $2\frac{1}{4}$ by 4 by 7 ins. high—the height being about $\frac{3}{4}$ in. less than the height of Nessler jars—through which two chambers $1\frac{3}{8}$ ins. diameter and $1\frac{3}{4}$ ins. between centers are bored lengthwise—the chambers being of such diameter as to just receive the jars.

To one end of the block is fastened the base, which is $\frac{1}{4}$ in. thick and through which two $\frac{7}{8}$-in. holes are bored concentric with the chambers, thus forming a shoulder which supports the jars and also exclude light from the sides of the tubes. To prevent shadows and give better lighting the holes in the base are beveled outward at an angle of 45°. The construction will be apparent by reference to Fig. 125. The interior of the chamber is painted dead black.

(a) For Determination of Titanium Insoluble in Hydrochloric Acid

Procedure.—Dissolve 5 grams of steel in 100 ml. of dilute hydrochloric acid (one of concentrated acid to two of water) by boiling gently. Wash off the cover and wash down the sides of the beaker with water and filter out the slight insoluble residue, washing with hot water and dilute hydrochloric acid until free from iron. For filtration it is advisable to use either a close-grained paper or double rapid-filtering papers such as S. & S. No. 589 white ribbon.

Ignite the residue *gently* in a platinum crucible to burn off carbonaceous matter. Treat the residue in the crucible with a mixture of 3 ml. dilute sulfuric acid (1 : 1), 2 or 3 ml. hydrofluoric acid, and a few drops of nitric acid. Heat and evaporate to fumes of sulfuric anhydride to complete expulsion of hydrofluoric acid.

Cool, add a few ml. of water and heat until the solution is perfectly clear. The ignited residue may also be rapidly and completely brought into solution by fusion with about 3 grams of potassium pyrosulfate and dissolving the fusion in water and sulfuric acid.

In either case wash the contents of the crucible into one of a pair of Nessler jars and dilute with cold water nearly to the 50-ml. mark, and in the other jar place an equal volume of distilled water.

Place the jars in the colorimeter and observe if the sample solution is colorless. If the sample solution is colored slightly yellow by iron, the water in the standard tube should be brought to the same color by addition of a few drops of a ferric solution. For this purpose a solution of ferric ammonium sulfate, 30 grams per liter, is very convenient.

[41] Thornton recommends the Dunnington's colorimeter as a more convenient instrument than Barton's block (see W. M. Thornton, "Titanium," A.C.S. Monograph Series No. 33, N. Y. Chem. Cat. Co., 1927, p. 130. (Private communication to the Editor, W. W. S.)

If the work up to this point has been carefully performed, the addition of ferric solution will usually be unnecessary; and if more than a few drops of ferric solution are required the analysis should be rejected and a new sample started. After adjusting the color—if necessary—bring the volume of solution in both jars to the 50-ml. mark.

The volumes now being equal and the solutions practically colorless, add 2 ml. of the peroxide solution to each. If the sample contains titanium even in minute quantity it will be indicated by the immediate development of a yellow color.

Match the colors by running into the standard jar freshly prepared *dilute standard* titanium solution, keeping the volumes equal by adding an equal quantity of water to the sample, placing the jars in the colorimeter for comparison colors.

As before stated, each ml. of the dilute standard solution is equal to 0.001% titanium when using a 5-gram sample.

The determination may be made in less than an hour and requires little attention.

(*b*) For Determination of Titanium Soluble in Hydrochloric Acid

For the determination of soluble titanium the filtrate from the insoluble titanium residue obtained as before described may conveniently be used.

Dilute the solution in which the iron is already in the ferrous state to 180 ml. Add 10 ml. of alum solution made by dissolving 40 grams of crystallized alum in a liter of water.

The aluminum here added is subsequently precipitated as alumina with the titanium and serves to collect quickly the exceedingly small precipitate of titanium hydroxide and facilitate its separation from the solution by filtration.

Heat the solution to about 90° C. and add ammonia or ammonium carbonate solution, stirring constantly until a slight permanent precipitate is produced. Add dilute hydrochloric acid (1 : 1) drop by drop from the wash bottle until the precipitate is just redissolved and the solution perfectly clear; then add 1 ml. more of the dilute hydrochloric acid.

Add 3 ml. of phenylhydrazine dissolved in 10 ml. hot water, which will precipitate the titanium and aluminum. Stir thoroughly and filter immediately on a 7-cm. filter paper in a Büchner funnel, using suction. Wash thoroughly with hot water.

Calcine the precipitate *gently* in a platinum crucible to destroy organic matter and dissolve the residue exactly as described under (*a*), except that 6 ml. of dilute sulfuric acid is used instead of 3 ml.

The solution, which has a very light yellow, or greenish-yellow color, is transferred to one of a pair of Nessler jars and diluted to the 50-ml. mark. About 40 ml. of water are placed in the other jar and the color of the sample solution exactly matched by addition of ferric ammonium sulfate and copper sulfate solutions, which are conveniently delivered from burettes.

For matching the original color of the solution nearly saturated solutions of ferric ammonium sulfate and copper sulfate are suitable.

Only a few drops of such solutions are required, but it is frequently necessary to use both blue and yellow to match the greenish-yellow tone of the sample solution.

The standard is finally diluted to the 50-ml. mark. The volumes now being equal and identical in color, add to each 2 ml. peroxide solution to develop the titanium color and finish the determination as before described under (*a*).

(*c*) For Determination of Total Titanium

The total titanium is given by the sum of the insoluble and soluble titanium determined as under (*a*) and (*b*); but if desired may be determined in one operation.

To determine total titanium, dissolve as before in hydrochloric acid and without filtering proceed as directed under (*b*) for determination of soluble titanium.

See also method of C. R. McCabe, J. Ind. Eng. Chem., **5**, 734–6; 872 (1913).

DETERMINATION OF TITANIUM WHEN INTERFERING ELEMENTS ARE PRESENT

If chromium, vanadium or molybdenum is present in the steel, fuse the residue insoluble in hydrochloric acid or the calcined phenylhydrazine precipitate containing the interfering element with a mixture of sodium carbonate and a little sodium nitrate.

Dissolve the fusion in water and filter. The residue on the filter will contain the titanium, free from interfering elements. Bring the residue into sulfuric acid solution by methods before described and determine the titanium as usual.

COLORIMETRIC DETERMINATION OF TITANIUM WITH THYMOL [42]

Principal and Preliminary Considerations.—Titanium dioxide dissolved in sulfuric acid is colored red by addition of thymol, the depth of color being directly proportional to the amount of titanium present. The intensity of the color is claimed by Lenher and Crawford to be twenty-five times that produced by hydrogen peroxide with the same amount of titanium.

As in case of hydrogen peroxide, fluorides destroy the color, hence must be absent. Dilution with water has no effect until the concentration of sulfuric acid falls below 79.4 (i.e., sp.gr. 1.725). The color then fades in direct proportion to dilution. Warm solutions are lighter in color than cold solutions with the same amount of titanium, hence the standard and the sample compared must have the same temperature. The color fades on heating but returns on cooling. The temperature should be kept below 100° C. Chlorides, phosphates and tin seem to have no effect. Tungsten, WoO_3, interferes, as it intensifies the color of the solution in direct proportion to the amount present; hence it must be removed or allowance made by adding an equivalent amount to the standard or subtracting the equivalent blank.

Special Reagents. *Thymol Solution 1%.*—The thymol is dissolved in a little glacial acetic acid containing 10% ethyl alcohol, and this solution added

[42] V. Lenher and W. G. Crawford, Chem. News **107**, 152 (1913).

to concentrated sulfuric acid. Addition of the thymol directly to the acid would produce a colored solution. The reagent should be kept protected from strong light, otherwise it will become colored.

Apparatus.—See Colorimetric Determination of Titanium with Hydrogen Peroxide, Figs. 124, 125, also Fig. 59.

Procedure.—About 0.3 gram of the material is fused with potassium acid sulfate, $KHSO_4$, and the melt dissolved in concentrated sulfuric acid. Enough thymol reagent is added so that there is present at least 0.006 gram thymol for every 0.0001 gram TiO_2. Concentrated sulfuric acid is added to bring up the volume to 50 or 100 ml. in a Nessler tube exactly as in the case of the colorimetric determination of titanium with H_2O_2. The depth of color is compared with a standard solution of titanium dissolved in a concentrated sulfuric acid added to 5 ml. of thymol solution made up to a convenient volume with concentrated sulfuric acid. The procedure is the same as described in the H_2O_2 method.

NOTE.—Vanadium also produces a color with thymol under conditions above.

THE ANALYSIS OF TITANIFEROUS ORES [43]

DETERMINATION OF TITANIUM

Decompose the ore by fusion with potassium pyrosulfate, dissolving the fusion in water, hydrochloric and sulfuric acids. If an insoluble residue remains, filter it out. Calcine the residue, add a few drops of sulfuric acid and sufficient hydrofluoric acid to dissolve silica, evaporate to fumes of sulfuric anhydride and then heat to redness.

If a residue now remains, bring it into solution directly in acids or fuse with a little potassium pyrosulfate, then dissolve and finally add the solution to the main solution obtained as before described.

If desired, the sample of ore can first be partially dissolved in hydrochloric and sulfuric acids, and the insoluble residue then fused with potassium bisulfate or treated with sulfuric and hydrofluoric acids.

Some ores may be completely decomposed by a mixture of nitric, hydrofluoric and sulfuric acids, evaporating to fumes of sulfuric anhydride in a platinum dish to free the solution from nitric and hydrofluoric acids.

The complete decomposition of the sample having been accomplished, the titanium in the solution is determined by the volumetric methods.

DETERMINATION OF IRON IN PRESENCE OF TITANIUM

Determination of Fe_2O_3.—The sample is decomposed as directed under the determination of titanium.

[43] Method of Analysis used in the laboratories of the National Lead Company—Titanium Division.

The final acid filtrate from the above method of decomposition is passed through a Jones reductor and titrated with standardized 0.1 N potassium permanganate. The titration will include the total Fe and TiO_2 present in the ore. The amount of TiO_2 determined in the previous analysis is calculated to its equivalent in ml. of 0.1 N $KMnO_4$ and subtracted from the total reading of the titration. The remainder is equivalent to the total Fe as FeO and Fe_2O_3. The FeO is determined separately.

Determination of FeO.—Weigh 0.5 gram of the finely-ground ore into a 500 ml. wide-mouth Erlenmeyer flask and wet with a few ml. of water. Insert a funnel with a 6-mm. diameter×55 mm. stem into the mouth of the flask. Insert a tube through the funnel into the flask and pass CO_2 through this tube into the flask throughout the determination. Add 50 ml. 1 : 1 H_2SO_4 and 20 ml. concentrated HCl through the funnel and boil gently to the appearance of SO_3 fumes. Boil an additional two minutes. Cool, add 100 ml. water, remove the funnel and titrate the ferrous iron with standardized 0.1 N $KMnO_4$.

DETERMINATION OF SILICA

This determination is conveniently combined with the determination of titanium, the ore being preferably decomposed by fusion with potassium bisulfate. The fusion is dissolved and evaporated with excess sulfuric acid to fumes of sulfuric anhydride and the silica determination finished as usual—weighing, volatilizing with hydrofluoric acid, etc. If the ore contains quartz or a silicate undecomposable by treatment with potassium bisulfate and hydrofluoric acid, the residue filtered from the sulfuric acid solution should be fused with sodium carbonate and the silica then determined as usual.

In the determination of silicon, a radiator for volatilizing silicon fluoride, such as that recommended by Whitfield (A. A. Blair, "The Chemical Analysis of Iron," 1918, p. 17, J. B. Lippincott Company), W. F. Hillebrand (U. S. Geol. Survey, Bull. **700**, 33 (1919)), or the simple nickel crucible radiator, as proposed by Thornton (W. M. Thornton, J. Ind. Eng. Chem., **3**: 419–20 (1911); W. M. Thornton, "Titanium" A.C.S. Monograph Series No. 33, N. Y. Chem. Cat. Co., 1927, p. 125) is useful.

DETERMINATION OF ALUMINA

Prepare a solution of 1.0 gram of ore as indicated under the determination of titanium.

Make up the final filtrate to 400 ml. and cool to 10–15° C. Add 80 ml. of 6% cupferron solution, slowly with constant stirring. This will precipitate most of the heavy metals including iron and titanium, but not calcium. Filter the precipitate and wash 10–12 times with cold 10% HCl containing a few drops of cupferron. Collect the filtrate in a 2 l. beaker, add 50 ml. concentrated HNO_3 and evaporate to SO_3 fumes. Add small portions of HNO_3 until the solution is free of organic matter.

Add 5 gms. NH_4Cl to the diluted solution. Make just alkaline (methyl red) with NH_4OH and boil the solution 1–2 minutes. Filter and wash thoroughly with hot 2% NH_4Cl solution. Ignite and weigh as Al_2O_3.

Since the alumina precipitate may be contaminated by phosphoric anhydride (P_2O_5), determine it by analysis and correct the alumina determination accordingly.

DETERMINATION OF PHOSPHORUS

Phosphoric acid may be separated from titanium oxide by repeatedly fusing the ore with alkali carbonate and extraction of alkali phosphate with water.

The determination of other constituents of the ore are conducted by the usual methods of ore analysis.

See also Ridsdale's work (N. D. Ridsdale, Chem. News **120**, 219 (1920); Proc. Cleveland Inst. Eng. **55**, 162 (1919)) on the determination of phosphoric acid in titaniferous iron ores.

DETERMINATION OF IRON, TITANIUM AND ZIRCONIUM IN BAUXITE

In the Bureau of Standards Journal of Research, Vol. 1, No. 1, July, 1928, pages 91 to 104, there appears an article on the general analysis of bauxite by G. E. F. Lundell and J. L. Hoffman.

This article is important as a contribution to the literature on bauxite giving details of a complete accurate method of analysis including the determination of titanium. The separation of titanium is accomplished by oxidizing titanium in solution to peroxide by addition of hydrogen peroxide and then separating the zirconium as phosphate.

In the course of the general analysis the iron, titanium and zirconium are precipitated together by addition of a mixture of sodium hydroxide and sodium peroxide in solution, digesting for an hour on steam bath, filtering out and washing, thus separating from chromium, vanadium and phosphoric acid.

The iron, titanium and zirconium are then determined as follows: " Dissolve the reserved precipitate in 25 ml. of hot dilute HCl (1 : 2), add 5 g. of tartaric acid, dilute with water to a volume of 200 ml., and neutralize with NH_4OH. Add 2 ml. of HCl per 100 ml. of solution, heat to boiling and saturate with H_2S. Allow to cool and filter off any platinum sulfide which may have separated and wash with a 1% solution of H_2SO_4 saturated with H_2S.

" Render the filtrate slightly ammoniacal, pass in a rapid stream of H_2S for five minutes, and digest at the side of the steam bath (40° C.) 15 to 30 minutes. Filter and wash with a dilute solution of $(NH_4)_2S$ (5 : 95) containing 5 g. of NH_4Cl per liter. Reserve the filtrate (*D*).

" Dissolve the iron sulfide in hot dilute HCl (1 : 1) to which has been added a little $KClO_3$, evaporate to dryness, take up in 25 ml. of dilute HCl (5 : 95), and add $KMnO_4$ until the usual pink color is obtained. Reduce with $SnCl_2$ and titrate slowly with a standard solution of $KMnO_4$, as in the Zimmermann-Reinhardt method.

" The filtrate (*D*) contains the titanium and zirconium. Acidify this solution with H_2SO_4, dilute to 200 ml., adjust the acidity so that the solution contains 10 ml. of H_2SO_4, sp.gr. 1.84 per 100 ml., and cool in ice water. It is unnecessary to destroy tartaric acid. Precipitate the titanium and zirconium with an excess of a cold 6% water solution of cupferron. An excess of the

precipitant is indicated by the formation of a fine white precipitate which redissolves, instead of a curdy one which persists. Stir in a little macerated paper, allow to settle for five minutes, filter by suction through a paper and cone, and test the filtrate for complete precipitation. Thoroughly wash the precipitate with cold dilute HCl (1 : 9). Transfer to a weighed platinum crucible, carefully dry, then cautiously char and burn the carbon, and finally heat at approximately 1200° C. over a blast lamp or its equivalent. Cool in a desiccator, weigh as ZrO_2+TiO_2, and repeat the ignition until constant weight is obtained. The correction of the weighed oxides for SiO_2 by direct treatment with H_2SO_4 and HF is a difficult procedure and is well nigh impossible if the residue is large. The amount of SiO_2 is usually small and can be determined if desired by evaporating the H_2SO_4 solution of the pyrosulfate melt obtained in the next step to fumes of H_2SO_4, diluting so that the solution contains 10% of the acid by volume, and recovering the SiO_2 by filtering and washing.

"Fuse the precipitate of TiO_2 and ZrO_2 with a small amount of $K_2S_2O_7$, dissolve the melt in 50 ml. of dilute H_2SO_4 (1 : 9), add sufficient H_2O_2 to oxidize all of the titanium (an excess does no harm), add 0.5 g. of $(NH_4)_2HPO_4$, allow to stand at the side of the steam bath (40° C.) overnight, filter, wash with a 5% solution of NH_4NO_3, ignite and weigh as ZrP_2O_7. Calculate to ZrO_2 and subtract from the total weight of TiO_2+ZrO_2. As a check, titanium can be determined colorimetrically, before the precipitation of zirconium. In very accurate analyses the ZrP_2O_7 should be fused with a little $K_2S_2O_7$, the melt dissolved in 10% H_2SO_4 as before, and the precipitation repeated. More phosphate must be added in the second precipitation, and an excess of H_2O_2 should be present at all times."

ANALYSIS OF MIXED PIGMENTS CONTAINING TITANIUM DIOXIDE

Weigh one gram sample into a 400-ml. Pyrex glass beaker, add 10 grams ammonium sulfate and 40 ml. concentrated sulfuric acid (93%). Heat on hot plate for one-half hour and then increase the heat, as by placing the beaker directly over the coils of an electric hot plate and boiling for about 10 minutes. The solution should acquire a temperature of about 335° C.

Cool, dilute the solution to 300 ml., boil 20 minutes, filter while hot and wash residue and precipitate with 5% sulfuric acid. On the filter will be silica and undecomposed silicates and all the lead and barium as sulfates. This residue and precipitates can be analyzed by well-known methods if desired. The filtrate will contain the titanium, iron, aluminum, zinc and calcium.

To the filtrate while still hot add an excess of ammonia, filter and wash precipitate with hot water. Re-dissolve precipitate in hydrochloric acid (1 : 1) and again precipitate with ammonia. Filter and wash with hot water, combining filtrate with that from first separation. By this procedure the titanium,

iron and aluminum will have been separated from the zinc and calcium. The use of an excess of ammonia as described would tend to carry a little aluminum into solution but in the presence of titanium and iron substantially all the aluminum will be found in the precipitate. If desired, the filtrate can be tested for presence of aluminum and then used for determination of calcium and zinc.

The precipitate of titanium, iron and aluminum hydroxide is again redissolved in dilute hydrochloric acid and the titanium separated and determined as before described and with all precautions given under the head of "Gravimetric Method for the Determination of Titanium Dioxide in Pure Titanium Dioxide."

The filtrate after separation of the titanium can be used for determination of iron and aluminum if desired.

In case it is not desired to determine iron and aluminum separately, the hydroxides obtained after second separation by ammonia can be calcined and weighed as total oxides of titanium, iron and aluminum. The titanium can be determined by the volumetric method before given and deducted from total oxides thus giving the iron and aluminum together by difference.

NOTE.—A procedure for the systematic examination of titanium pigments has been adopted by the American Society for Testing Materials and is described in the "A.S.T.M. Standards," 1939, Part II, p. 683. The determination of titanium there described is substantially the same as given in this text. For the examination of pure titanium pigments this method is very satisfactory but cannot be used when the titanium pigment is mixed with other pigments containing iron. In such cases the more general method described on page 981 in connection with the volumetric method, second half of page 984 is satisfactory.

ANALYSIS OF TITANOX-B PIGMENT

Weigh 0.5 gram of titanium-barium pigment in a 400-ml. beaker, add 20 ml. H_2SO_4 and 10 grams $(NH_4)_2SO_4$ and dissolve over a Méker burner. When cool, dilute to 300 ml. add a few drops of concentrated HCl and boil for five minutes. Allow to stand overnight.

Filter through a double No. 42 Whatman paper, wash three times with hot 5% H_2SO_4 and then with hot water until free of TiO_2 (H_2O_2 test). Ignite the residue and weigh as $BaSO_4$. If silica is present remove by an HF treatment.

The filtrate from the $BaSO_4$ determination is evaporated to about 200 ml. and the titanium determined as described under Volumetric Method for the Determination of Titanium Dioxide in Pure Titanium Dioxide, p. 986.

ANALYSIS OF TITANOX-C PIGMENT

Titanium Oxide (TiO_2).—Weigh 0.5 gram of the titanium-calcium pigment into a 250-ml. Pyrex beaker. Add 10 grams of ammonium sulfate and 25 ml. of concentrated sulfuric acid. Cover the beaker with a watch glass and digest the whole on the hot plate to complete solution. After cooling, carefully dilute the solution to a volume of about 200 ml. with distilled water, heat to boiling, transfer immediately to the reductor and determine the titanium as under Volumetric Method, p. 984.

Total Calcium Oxide (CaO).—Weigh 0.5 gram into a 250-ml. beaker. Add three grams of ammonium chloride and sufficient water to moisten the mixture. Add 25 ml. of concentrated hydrochloric acid and boil for 15 minutes. Add one hundred ml. of hot distilled water; boil the solution for 5 minutes and then filter through double No. 42 Whatman papers, using a small amount of paper pulp, and wash three times with hot distilled water. Wash the residue back into the original beaker, add 3 grams of ammonium chloride and 20 ml. of hydrochloric acid and boil for 15 minutes. Dilute the solution with 100 ml. of water, boil and filter through the original filter paper, receiving the filtrate in the first filtrate. Wash the precipitate six times with hot distilled water. Make the combined filtrate slightly alkaline to litmus with ammonia, boil five minutes and filter through double No. 42 Whatman papers. After washing six times with hot water reject the precipitate. Evaporate the filtrate to a volume of about 400 ml., add slowly 25 ml. of a saturated solution of ammonium oxalate to the hot solution from a pipette, and boil the solution for five minutes and allow to stand in a warm place overnight. Filter the precipitate of calcium oxalate and wash with hot water to remove all of the ammonium oxalate (usually 10 to 12 washings). Wash the calcium oxalate precipitate back into the beaker with hot water, 15 ml. of 1 : 1 sulfuric acid is added and the whole diluted to about 300 ml. The solution heated to about 80° C. is titrated with 0.1 N potassium permanganate to a pink color. The filter paper is carefully unfolded and placed in the solution and the titration continued after stirring, until a pink color is reached. The oxalate so titrated is calculated to calcium oxide, CaO.

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TUNGSTEN [1]

W., *at.wt.* 184.0; *sp.gr.* 19.3; *m.p.* 3370° C.; *oxides,* WO_2 (brown); WO_3 (yellow); *acids,* H_2WO_4, ortho tungstic; $H_2W_4O_{13}$, meta tungstic

The element occurs in rocks high in silica. It is found commonly associated in form of tungstate with calcium, copper, iron and manganese. It occurs as sulfide, WS_2. The more important minerals are ferberite, $FeWO_4$; hübnerite, $MnWO_4$; wolframite, $(FeMn)WO_4$; scheelite, $CaWO_4$; cuproscheelite, $(CaCu)WO_4$; tungstenite WS_2; stolzeit, $PbWO_4$. In addition to the evaluation of the tungsten ores the chemist is called upon to determine tungsten in concentrates, in alloys—steels, ferro-tungsten, silico-tungsten, tungstic oxide, tungsten powder, alkali tungstates.

DETECTION

Minerals.—The finely powdered material is decomposed by treating with mixed acids according to the procedure given on page 1005. Tungsten is precipitated with cinchonine, the precipitate filtered off and dissolved in ammonium hydroxide, then acidified with hydrochloric acid and reprecipitated with cinchonine as described.

Tungsten oxide may be confirmed as follows:

1. The residue is suspended in dilute hydrochloric acid and a piece of zinc, aluminum, or tin placed in the solution. In the presence of tungsten a blue-colored solution or precipitate is seen, the color disappearing upon dilution with water.

2. A portion of the precipitate is warmed with ammonium hydroxide and the extracts absorbed with strips of filter paper.

(*a*) A strip of this treated paper is moistened with dilute hydrochloric acid and warmed. In the presence of tungstic acid a yellow coloration is produced.

(*b*) A second strip of paper is moistened with a solution of stannous chloride. A blue color is produced in the presence of tungsten.

[1] Tungsten was discovered by Scheele (1781) in the mineral calcium tungstate named scheelite after the discoverer. The metal stands at the top of the list in melting point (3370° C.), a property that led to its use in filaments of the incandescent lamp. High speed cutting tools contain 18–20% of tungsten. Tungsten steel is used in springs, valves, axles, magnetos, phonograph needles, contact points, spark plugs, steel rails and numerous products where strength, hardness, durability, resistance to corrosion, high melting point are essential. The hardest cutting tool, carboloy, is the carbide of tungsten (W_2C). Sodium tungstate is used as a mordant and to fireproof fabrics.

(c) A third strip dipped into cold ammonium sulfide remains unchanged until warmed, when the paper turns green or blue if tungsten is present.

Iron, Steel and Alloys.—These decomposed with concentrated hydrochloric acid followed by nitric acid as directed under Solution of the Sample leave a yellow residue in the presence of tungsten. If this residue is digested with warm ammonium hydroxide and the extract evaporated to dryness a yellow compound, WO_3, will remain if tungsten is present. This oxide may be reduced in the reducing flame to the blue-colored oxide.

ESTIMATION

The material should be finely ground for analysis. The mineral hübnerite and scheelite decompose easily, ferberite not so readily and wolframite with difficulty. The alloys require special treatment according to the composition.

In analytical procedures some tungsten as WO_3 may be found with the SiO_2 residue. The oxide is readily volatile at 900° C. The residue of WO_3 (and SiO_2) should be ignited to not over 750° C. The tungsten remaining in solution from the silica and tungsten residue will not precipitate completely with iron and alumina when NH_4OH is added to the solution; unless provision has been made for its previous removal, some may pass into solution of the alkaline earth group causing error there. Separation of tungsten must be made in the initial steps of analysis.

Details of preparation and solution of the materials containing tungsten follow later.

SOLUTION OF THE SAMPLE

For solution of the sample the following facts should be kept in mind regarding solubilities.

The metal is practically insoluble in HCl and H_2SO_4. It is slowly attacked by HNO_3, aqua regia and by alkalies. It is readily soluble in a mixture of HNO_3 and HF to form WF_6 or WOF_4.

Oxides.—WO_2 is soluble in hot HCl and in hot H_2SO_4 (red soln.) also in KOH (red soln.). The oxide WO_3 is scarcely soluble in acids, but is readily soluble in KOH, K_2CO_3, and in NH_4OH, $(NH_4)_2CO_3$, $(NH_4)_2S_x$ unless strongly ignited, when it is insoluble. Both the acid and the alkali solutions deposit the blue oxide on standing.

Acids.—Ortho tungstates. A few are soluble in water and in acids. The alkali salts only slightly soluble. The meta tungstates are easily soluble in water. Tungstates are precipitated from alkali salts by dilute H_2SO_4, HCl, HNO_3, as yellow $WO_3 \cdot H_2O$ or white $WO_3 \cdot 2H_2O$. Meta tungstates are not precipitated by cold acids, but are precipitated by boiling and by long standing.

Solution of Minerals.—The material may be decomposed by acid treatment as described on page 1005. Use of a fusion as a means of decomposition of

tungsten ores preliminary to either the qualitative detection or the quantitative determination of tungsten may also be employed, p. 1010. The precipitation of tungsten by boiling with acids in presence of considerable amounts of alkali salts (such as result from acidification of a fusion) is feasible if the solution is diluted sufficiently. When the amount of tungsten present is small, and especially if the ore contains much phosphorus, there is small likelihood that any of the tungsten will be precipitated. The use of cinchonine is necessary in order completely to precipitate tungsten under these conditions; ferric iron has a retarding effect on the cinchonine precipitation.

SEPARATIONS

Separation of Tungsten from Silica.—The oxide of tungsten, as ordinarily obtained, is frequently contaminated with silica. The removal of silica is accomplished by heating the mixture in a platinum dish with sulfuric and hydrofluoric acids and volatilizing the silica. After taking to dryness and igniting gently, the last traces of sulfuric acid are expelled by adding ammonium carbonate and again igniting.

The dehydration of silica by slow evaporation with $HClO_4$, heating to fumes of $HClO_4$ and a temperature of 205° C. is an effective procedure.

In presence of small amounts of silica (0.1 to 0.2%) and large amounts of tungsten (75 to 85%) J. A. Holladay recommends evaporation with sulfuric and phosphoric acids, filtration to remove the bulk of the tungsten, and subsequent ignition and volatilization with sulfuric and hydrofluoric acids.

Separation from Tin.—The weighed residue is mixed with six to eight times its weight of ammonium chloride (free from non-volatile residue) in a platinum crucible, placed in a larger crucible, both vessels being covered. Heat is applied until no more vapors of ammonium chloride are evolved. Additional ammonium chloride is added and the treatment is repeated three times. The fourth treatment is followed by weighing of the residue and the treatment repeated once more. If no further loss of weight takes place it is assumed that all the stannic oxide has been driven off. The inner crucible is now placed directly over the flame and heated to dull redness for a few minutes and the oxide, WO_3, weighed.

Separation of Tungsten from Arsenic and Phosphorus.—Both arsenic and phosphorus may be precipitated by cold magnesia mixture in an ammoniacal solution, tungsten remaining in solution. The separation of arsenic is difficult, as it is tenaciously retained by tungsten as a complex salt. The following process is outlined by Kehrmann.[2]

One to 2 grams of the sample are fused with twice as much sodium hydroxide as is required to combine with the arsenic oxide, the resulting cake is dissolved in a little water and boiled in an Erlenmeyer flask for half an hour. After

[2] F. Kehrmann, Ber., 20, 1813 (1887).

cooling, three times as much ammonium chloride as is needed to form chlorides with the alkalies present is added, and then ammonium hydroxide equal to one-fourth the volume of the solution under investigation, followed by sufficient magnesia mixture, added cold, drop by drop with constant stirring. After settling several hours, the solution is filtered and the residue washed with a weak solution of ammonia and ammonium nitrate. It is advisable to dissolve the residue in dilute acid and repeat the precipitation several times. The filtrates containing the tungsten are combined and concentrated by evaporation if necessary.

NOTE.—Low values for phosphorus are apt to be obtained when the material to be tested contains WO_3 and is fused with NaOH, Na_2O_2 etc.

Volatilization of Molybdenum with Dry Hydrochloric Acid Gas. Pechard's Process.[3]—The procedure depends upon the fact that molybdenum oxide heated in a current of dry hydrochloric acid gas at 250 to 270° C. is sublimed, whereas tungsten is not affected.

The oxides of the two elements, or their sodium salts, are placed in a porcelain boat and heated in a hard glass tube, one end of which is bent vertically downward and connected with a Peligot tube containing a little water. A current of dry hydrochloric acid gas is conducted over the material, heated to 250 to 270° C. From time to time the sublimate of molybdenum ($MoO_3 \cdot 2HCl$) is driven towards the Peligot tube by careful heating with a free flame. This enables the analyst to observe whether any more sublimate is driven out of the sample and to ascertain when the tungsten is freed of molybdenum. From one and a half to two hours are generally sufficient to accomplish the separation. If sodium salt is present it is leached out of the residue, and is then ignited to WO_3. Molybdenum may be determined in the sublimate.

Separation from Vanadium.[4]—Tungstic and vanadic acids are precipitated with $HgNO_3$ and HgO, the moist precipitate dissolved in HCl and the solution largely diluted; WO_3 is precipitated free from vanadium.

Separation from Titanium.—Powell, Schoeller and Jahn found that the following method gives quantitative results.[5]

Caustic-soda Method.—The mixed oxides (about 0.25 g.) are fused with 3 g. of Na_2CO_3 in platinum over a Teclu burner for 20 minutes. The crucible and contents, when cold, are placed in a nickel dish containing 10 g. NaOH in 50 ml. of water. The covered dish is placed on a boiling water bath for 2–3 hrs., and the water lost by evaporation is replaced. The crucible is cleaned and rinsed with 50 ml. of hot water. The solution is allowed to cool or to stand over night. The residue (I) is washed with half-saturated NaCl solution.

The filtrate is treated with diluted HCl until phenolphthalein is decolorized, then heated on the water bath, and the red color is discharged from time to time with a few drops of the acid. The precipitate (II) is washed in the same way as (I).

Precipitates I and II are treated with a little normal HCl, and after dilution to 100 ml., the titania is recovered by heating, making the solution ammoniacal,

[3] E. Pechard, Comp. rend., 114, 173 (1891).
[4] Friedheim, Chem. News, 61, 220 (1890).
[5] Analyst, 60, 506 (1935).

filtering, washing with NH_4NO_3 solution, and ignition. Unless the precipitate is small, it is leached with dilute acid, reprecipitated, etc.

The tungsten in the combined filtrates from the titania precipitate is recovered in the usual manner.

Separation of Tungsten from Iron.—The procedure is given under Solution of the Sample, of Steel and Alloys The impure oxide WO_3 is fused with Na_2CO_3 and the melt extracted with water. $Fe(OH)_3$ remains on the filter. The filtrate is evaporated to dryness with HNO_3 and the residue extracted with water. The insoluble WO_3 is washed with 2% HCl solution, then dissolved in NH_4OH and tungsten determined in the solution.

Separation of Tungsten from Uranium.[6]—The sample is evaporated with nitric acid nearly to dryness, 5 ml. of HNO_3 is added and the uranium is dissolved out by extraction with ether.

Separation of Tungsten from Lead.—In the acid attack if sulfates are present lead sulfate will remain with tungsten. Tungsten is separated by dissolving with NH_4OH. Lead remains in the residue. Any entrained lead in the tungsten filtrate may be separated by precipitation as sulfide by addition of ammonium sulfide, tungsten remaining in solution.

GRAVIMETRIC PROCEDURES FOR DETERMINING TUNGSTEN

Since there is no highly commendable volumetric procedure for determining tungsten, the gravimetric methods are preferred.

The element is determined as tungstic oxide, WO_3. It may be isolated preferably by precipitation with cinchonine, or in the form of tungstic acid, ammonium tungstate, or as mercurous tungstate, in the usual course of analysis, all of which forms may be readily changed by ignition to the oxide, WO_3.

The oxide, WO_3, may be contaminated with Ag, Fe, Mo, P, Cr, Si, Sn, Sb, Cb or Ta compounds. The pure oxide upon fusion with Na_2CO_3 and extraction with water leaves no residue. Na, K and NH_4 salts, P, As, and Mo retard precipitation. A temperature of 750° is necessary for dehydration of tungstic acid. The ignition temperature should not exceed 850° C. due to the volatility of WO_3.

THE DETERMINATION OF TUNGSTEN IN ORES AND CONCENTRATES[7]

Determination of Tungsten. ***Method A.***—One g. of the dried agate ground sample (200 mesh, double-screened) is transferred to a 600-ml. beaker; 5 ml. of water are added and the beaker manipulated to distribute the ore evenly over its bottom. In case of low grade ores, a larger sample is employed.

[6] C. A. Pierle, Jour. Ind. Eng. Chem., 12, 61–63 (1920).

[7] Methods of the Electro Metallurgical Co. contributed by Thos. R. Cunningham.

Two hundred ml. of HCl (sp.gr. 1.19) are added and the covered beaker and its contents are heated for about one hour, with occasional stirring to prevent the formation of crusts, at a temperature not exceeding 60° C. The solution is then boiled down to a volume of 50 ml. Five ml. of nitric acid, sp.gr. 1.42, are then added and the boiling continued until the volume has been reduced to 10 or 15 ml.

The clock-glass and the sides of the beaker are rinsed with a jet of water and the solution is diluted with hot water to approximately 500 ml. Five ml. of cinchonine solution (125 g. cinchonine dissolved in a mixture of 500 ml. of HCl sp.gr. 1.19 and 500 ml. of water) and some ashless paper pulp are added and the liquid is digested on a hot plate or water bath at 60–70° C. with occasional stirring, for 30 minutes or longer if convenient.

The tungstic acid precipitate is allowed to settle and the supernatant liquid is decanted off through an 11-cm. paper containing some paper pulp. After having washed the precipitate three times by decantation with hot cinchonine wash solution (10 ml. of "cinchonine solution" to 1 liter of warm water), it is transferred to the paper and washed thoroughly with the hot cinchonine wash solution, and finally from 6 to 8 times with warm 2% HCl to remove most of the cinchonine.

Provided the sample has been very finely pulverized it is usually possible to decompose completely scheelite with the exception of a siliceous residue and any tin present as SnO_2. Wolframite and ferberite are more resistant to the acid treatment and from 0.3 to 0.5% of tungsten remains unattacked in the insoluble residue. This is particularly true of Chinese wolframites. The acid treatment and dilution with water causes the precipitation of nearly all of the tungsten as orange-yellow tungstic acid, but the use of cinchonine is necessary to insure the precipitation of the last traces.

The tungstic acid precipitate and the paper on which it was filtered are next transferred back to the original 600-ml. beaker. Twenty-five ml. of boiling water are introduced and the filter paper is beaten to a pulp by means of a glass stirring rod. Five ml. of ammonia, sp.gr. 0.90, (sufficient to give a *slight* excess) are then added and the solution is warmed gently for about 10 minutes. The sides of the beaker are washed down with warm "ammonia wash solution" (100 ml. of ammonia of sp.gr. 0.90 and 10 ml. HCl of sp.gr. 1.19 per liter) and the liquid is stirred well and filtered on an 11-cm. paper. The filtrate is collected in a 600-ml. beaker and the original beaker and the filter paper are washed 10 times with warm "ammonia wash solution." The filter paper is next washed 5 or 6 times with hot 10% HCl to remove iron, from 8 to 10 times with warm "ammonia wash solution" to dissolve any remaining tungstic acid and then thoroughly with hot 0.3% ammonium chloride solution. The total volume of the filtrate should not exceed 225 ml. The residue insoluble in ammonia is usually free from tungsten, but in order to be sure that such is the case it is reserved and treated as further described.

The ammoniacal filtrate will contain all or nearly all of the tungsten in the form of ammonium tungstate. The liquid is evaporated to a volume of about 10 ml., when 20 ml. of concentrated HCl and 10 ml. of concentrated HNO_3 are added and the solution is boiled down to a volume of about 15 ml. which will result in the precipitation of a large part of the tungsten. Three hundred and fifty ml. of hot water, a considerable amount of ashless paper pulp and 10

ml. of "cinchonine solution" are added and the liquid is stirred well and digested at 60–70° C. for about 30 minutes or until the precipitate has settled completely. The solution is filtered on an 11-cm. paper containing some ashless pulp and the precipitate is washed thoroughly with hot "cinchonine wash solution."

The precipitate is ignited in a large weighed platinum crucible at a very low red heat until all the carbon of the filter paper has burned completely. The presence of the paper pulp is essential since it causes the precipitate to form a porous, friable mass, easily penetrated by oxygen, thus rendering it fairly easy to burn off the carbon and oxidize the tungsten. If the ignition is made in a muffle furnace, introduction of a current of oxygen is advantageous. The temperature is then increased to 750° C. for about 5 minutes. After having allowed the crucible to cool, the precipitate is moistened with hydrofluoric acid and the solution evaporated to dryness to expel any silica. The crucible and its contents are then re-ignited for at least 15 minutes (to constant weight) at 750° C. Particular care should be exercised to burn the cinchonine precipitate at the lowest possible temperature until all carbon has been oxidized or loss of tungsten will occur. Long continued heating, or heating to a higher temperature than that specified should be avoided.

The residue left from the ammonia treatment may contain silica or undecomposed silicates, cassiterite (tin oxide), or titanium minerals. It will also contain any columbium or tantalum present in the ore. The residue is usually free from tungsten, but it is never safe to neglect testing it. The filter containing the residue is ignited in a *porcelain* crucible (if tin were present it would be reduced by the filter paper and ruin a platinum crucible). After having transferred the residue to a platinum crucible, 1 or 2 drops of concentrated sulfuric acid and several ml. of hydrofluoric acid are introduced and the solution is evaporated to the expulsion of fumes of sulfur trioxide to remove any silica. The residue is fused with 5 g. of sodium carbonate, and after it is cool, the fused mass is extracted with water and (unless perfectly clear) the resulting solution is filtered. The filtrate is acidified with HCl, boiled to expel carbon dioxide, diluted with warm water to 150 ml. and tested for tungsten by adding 5 ml. of cinchonine solution. If, at the end of several hours' digestion a precipitate of tungsten appears, it is filtered on a 9-cm. paper, washed with "cinchonine wash solution," dissolved in ammonia, and reprecipitated and weighed in the same manner as previously described.

If the insoluble residue is known to be low in silica the treatment with sulfuric and hydrofluoric acids may be omitted; then it is transferred from the porcelain crucible to a 30-ml. nickel crucible and fused with several g. of sodium peroxide. The melt, when cool, is dissolved in a slight excess of 10% HCl and tested as previously described.

The combined tungsten trioxide precipitates are tested for $Ta_2O_5-Cb_2O_5$, iron and molybdenum by the following procedure: To the crucible containing the ignited and weighed WO_3 there are added 10 ml. of a 20% NaCl solution and 2 g. of pure sodium hydroxide. The crucible is covered and the solution is warmed for 15–20 minutes after the WO_3 appears to have dissolved completely and then allowed to stand for several hours in a tray of ice water. Twenty-five ml. of a cold 20% solution of NaCl are added, the solution stirred well, filtered on a 3-cm. paper containing some ashless filter pulp and the residue

washed thoroughly with cold 20% sodium chloride solution. The filtrate is reserved and tested for Mo.

The paper and residue containing any iron and $Ta_2O_5+Cb_2O_5$ present are transferred to a 150-ml. beaker, 25 ml. of HCl (1 to 4) and 20 ml. of sulfurous acid added and after warming the solution for about 5 minutes it is diluted with boiling water to 100 ml. and allowed to stand for about ½ hour. The solution is filtered on a 9-cm. paper, the precipitate washed from 8 to 10 times with hot 5% HCl, ignited in platinum first at a low temperature then for 15 minutes at 750° C., cooled in a desiccator and weighed. All of the tantalum and columbium are not found in the tungsten precipitate so this test may not be used for the determination of total tantalum and columbium. Iron is determined in the filtrate by any of the usual procedures and calculated to Fe_2O_3.

When the ore is known to be free from $Ta_2O_5+Cb_2O_5$, the WO_3 precipitates may be fused with approximately 3 g. of Na_2CO_3 and the melt dissolved in 50 ml. of hot water. The solution is filtered on a 9-cm. paper containing a small amount of ashless pulp and any residue is washed thoroughly with hot water and ignited in the same platinum crucible in which the WO_3 was fused. The weight of the residue is deducted from that of the impure WO_3 precipitate. The filtrate is reserved and tested for molybdenum.

The alkaline filtrate (obtained as described in the 10th or 12th paragraph) having a volume of not more than 100 ml. (containing the tungsten and molybdenum) is transferred to a 250-ml. separatory funnel. One gram of tartaric acid is added and the solution made just acid with dilute sulfuric acid (1 to 1) and cooled to 15° C. Twenty-five ml. of 8% ferric sulfate solution and 10 ml. of 5% KCNS solution are added, the stoppered flask and contents are shaken vigorously for several minutes, then treated with 5 to 10 ml. of stannous chloride solution and again shaken vigorously for several minutes. Tungsten may precipitate upon the addition of the ferric sulfate solution but it does not interfere.

The stannous chloride reduces the iron from the ferric to the ferrous state and the molybdenum from the sexivalent to the quinquivalent or quadrivalent condition. The potassium thiocyanate reacts with the reduced molybdenum to give an amber or reddish-brown color to the solution, depending upon the amount of molybdenum present.

The solution is cooled to 15° C., 50 ml. of ether added and the separatory funnel is stoppered, shaken vigorously for several minutes, and allowed to stand until the liquid has separated into two distinct layers. The lower or acid layer, which will contain all of the tungsten present, is drawn off and discarded (if the lower layer should show any pink color it must be given a second treatment with ether), and the upper or ethereal layer, which will contain all of the molybdenum, is then drawn off into a 50-ml. comparison tube and diluted with ether to the 50-ml. mark. The Camp tube is stoppered with a soft cork to prevent evaporation of the ether, and its contents are mixed thoroughly by manipulating the tube in the usual manner. After standing for several minutes it is ready for comparison with the standard. The weight of molybdenum in the sample is then determined by comparing the intensity of the color of the ethereal solution of potassium molybdenum thiocyanate with the standard solution containing a known amount of molybdenum.

Any molybdenum found is calculated to MoO_3 and deducted. The weight of the impure WO_3 precipitate, less the weights of $Ta_2O_5+Cb_2O_5$, Fe_2O_3 and MoO_3 found, gives the weight of WO_3 in the sample. The weight of WO_3 is multiplied by 79.31 and divided by the weight of the sample taken to give the percentage of tungsten.

Preparation of the Standard for Comparison.—With a little practice it is not difficult to estimate approximately the percentage of molybdenum in the sample. Twenty-five ml. of 8% ferric sulfate solution are transferred to a 250-ml. separatory funnel and the standard molybdenum solution is added from a burette. The solution is diluted with cold water to approximately 100 ml. and the development of the molybdenum color and extraction are completed as described in the 15th to 18th paragraphs. It is advisable to allow the molybdenum solution to stand in the comparison tube for several minutes before comparing with the standard, as the intensity of the color sometimes changes at first but remains stable thereafter for several days and even longer (more than a week) if kept in the dark when not in use.

The percentage of molybdenum in the sample is then determined by comparing the intensity of the color of the ethereal solution of potassium-molybdenum thiocyanate with that of the standard. The darker of the two solutions (the sample and the standard) is diluted carefully with ether and mixed thoroughly until they match exactly. The amount of molybdenum per ml. in the standard is then figured and the calculation of the weight of molybdenum in the precipitate is obtained by multiplying the weight of molybdenum in each ml. by the number of ml. The following example illustrates the calculations: In comparing the standard with the sample, 3 ml. of standard molybdenum solution (1 ml.$=$0.0002 g. Mo) were used and diluted to 44 ml. with ether. Therefore: $3\times0.0002=0.0006$ g. Mo, or $0.0006/44=0.0000136$ g. Mo per ml.

The sample was diluted to 36 ml., hence $36\times0.0000136=0.00049$ g. Mo in the sample.

Solutions Required

Standard Molybdenum Solution.—1 ml.$=$0.0002 gram Mo. This solution is prepared by dissolving 0.430 g. of *pure* sodium molybdate in one liter of water containing 10 ml. of 1 : 1 sulfuric acid and mixing thoroughly. One hundred ml. of this solution are measured carefully by means of an accurately calibrated pipette into a 250-ml. beaker, 12 ml. of 1 : 1 sulfuric acid are added and the solution is put through a Jones reductor into a solution of ferric sulfate, and titrated with a standard solution 0.05 N in potassium permanganate. (1 ml. $=$0.0016 g. Mo.)

A blank determination is run on the reductor and the solution of ferric sulfate (this usually amounts to 0.3 ml.) by passing 100 ml. of 6% sulfuric acid and 150 ml. of water (the same amount as in the analysis) through the reductor in exactly the same way as the molybdenum solution, and titrating the liquid with permanganate. The amount of 0.05 N permanganate required to impart a pink tint to the liquid constitutes the blank to be deducted from the burette reading when standardizing the molybdenum solution.

5% KCNS Solution.—Prepared by dissolving 5 g. KCNS in 100 ml. of water.

8% Ferric Sulfate Solution.—80 g. of ferric sulfate are dissolved in 1 liter of 20% sulfuric acid. The presence of iron is essential in the preparation of

the standard, since it has been determined by experiment that the ethereal solution of potassium-molybdenum thiocyanate is more comparable and also more stable than when it is omitted. The iron appears to catalyze the processes involved in the development of the color.

Stannous Chloride Solution.—350 g. of $SnCl_2$ are added to 200 ml. of hydrochloric acid (1 to 1) in 500-ml. Erlenmeyer flask, the liquid boiled gently until the salt has almost dissolved, transferred to a liter bottle and diluted with freshly boiled water to 1000 ml. A few pieces of metallic tin are introduced to prevent oxidation.

Fusion Method. Method B.—This method is suitable for the determination of tungsten in wolframite and has the advantage that complete decomposition can be obtained in a few minutes. Samples of scheelite, ferberite and ores containing more than 2 or 3% silica are best analyzed by Method A.

One g. of the dried 100-mesh sample of wolframite is mixed thoroughly with 10 g. of sodium peroxide in a 40-ml. nickel crucible and the mixture covered with approximately 2 g. additional sodium peroxide. The contents of the crucible are fused carefully over the flame of a laboratory burner. The fusion is best accomplished by holding the crucible in a pair of tongs and *slowly revolving* it around the outer edge of the flame until the contents have melted down quietly. Care should be taken not to raise the temperature so rapidly as to cause spattering. When the fusion is molten a slight rotary motion is imparted to the crucible to stir up any unattacked particles of ore on the bottom or sides, the crucible and contents being maintained at a low red heat. Just before the completion of the fusion which requires four to six minutes, the temperature is increased to bright redness for a minute. If these directions are followed *carefully* a very quiet fusion without any spattering will be obtained.

When the crucible has partly cooled and with cover tightly on, it is tapped several times on an iron plate to loosen the melt in a solid cake. The cake is transferred to a 600-ml. covered beaker and dissolved in 100 ml. of cold water and the crucible is rinsed with a jet of warm water and the rinsings added to the beaker. The solution is immediately made acid with an excess of 20 ml. of concentrated HCl, care being taken to avoid loss by spattering. The liquid is diluted to a volume of 250 ml. and boiled for 5 or 6 minutes. This should result in the precipitation of the larger part of the tungsten as tungstic acid and the remainder is precipitated by the addition of 10 ml. of cinchonine solution. Some ashless paper pulp is added and the solution is further diluted with warm water to about 500 ml. and allowed to digest in a warm place for several hours or until the precipitation is complete.

The determination is completed as described under Method A beginning with the third and ending with the twelfth paragraph.

Provided the operations have been carried out properly the residue insoluble in ammonia should contain no tungsten. However, it should be ignited and tested for tungsten as described in the eighth paragraph under Method A.

METALLIC TUNGSTEN AND TUNGSTEN ALLOYS[8]

A. S. T. M. PROCEDURE[9]

FERROTUNGSTEN AND TUNGSTEN METAL

DETERMINATION OF TUNGSTEN

Solutions Required

Cinchonine Solution.—Dissolve 125 g. of cinchonine in a mixture of 500 ml. of HCl (sp.gr. 1.19) and 500 ml. of distilled water.

Cinchonine Wash Solution.—Dilute 30 ml. of the above solution to one liter.

Method.—Treat 1.0000 of the material passing a No. 100 sieve in a large (60-ml.) covered platinum crucible, or preferably a large dish, with 5 ml. of hydrofluoric acid; add nitric acid drop by drop, with heating, until the metal is dissolved. Add 15 ml. of sulfuric acid (1 : 1) and heat cautiously on a sand bath until dense fumes of sulfur trioxide are freely evolved. Allow to cool and transfer the residue to a 400-ml. beaker with water, finally wiping the dish with a piece of ashless filter paper. Rinse the crucible or dish with a little warm ammonia (1 : 1), some water and then a few ml. of hot hydrochloric acid (1 : 1). Repeat the treatment with ammonia, water and hydrochloric acid, the rinsings being added to the 400-ml. beaker. Dilute the contents of the beaker to about 150-ml. with water, add 10 ml. of hydrochloric acid (sp.gr. 1.19) and boil for 5 minutes. Remove from the source of heat and dilute to 350 ml. with water. Add 10 ml. of cinchonine solution, some ashless paper pulp and digest the solution at 80 to 90° C. with occasional stirring for 30 to 45 minutes or longer. When the tungsten precipitate has settled and the supernatant liquid is clear, filter on an 11-cm. paper containing a little ashless paper pulp. Wash thoroughly with hot cinchonine wash solution and finally several times with warm 1% hydrochloric acid. Gently ignite the filter and residue in the crucible or dish in which it was originally treated until the carbon is consumed. Add a few drops of nitric acid and dry on a water or sand bath. Ignite the covered crucible or dish for 5 minutes or longer at about 750° C. (to constant weight), cool and weigh. Ignitions may be made at about 750° C. in an electric muffle

[8] Draft of proposed revision of A. S. T. M. procedure, pp. 80–81, Chemical Analysis of Metals, 1936, supplied by Mr. T. R. Cunningham, chairman of the committee of revision. Published with the permission of the American Society for Testing Materials.

[9] From Methods of Chemical Analysis of Metals, pp. 80–81, Dec. 1936. Published by the American Society for Testing Materials, Philadelphia, Pa.

furnace. As WO_3 is slowly but steadily volatilized at temperatures above 750° C., serious error may result if this temperature is not strictly adhered to. Add about 5 g. of sodium carbonate, cover with an additional 1 or 2 grams of sodium carbonate and fuse, running the fusion around the sides of the crucible or dish to remove all WO_3. Dissolve the fusion in hot water, add alcohol, heat, filter and wash thoroughly with hot water. Place the filter in the crucible and ignite; add a little sodium carbonate and fuse again. Dissolve the fusion in water, filter and wash very thoroughly with hot water to remove the last traces of sodium carbonate; ignite in the same crucible or dish as at first, cool and weigh. The difference between the weight of the crucible or dish, plus the residue and the weight of the crucible or dish, plus impure tungstic oxide, multiplied by 79.31, gives the percentage of tungsten.

NOTE 1.—Fuming with perchloric acid may be substituted for fuming with sulfuric acid if desired. In this case, add 15 ml. of perchloric acid (60%) after the treatment with hydrofluoric and nitric acids, and evaporate to strong fumes of perchloric acid. Cool, add 50 ml. of water, transfer the solution to a 400-ml. beaker and proceed as in the case of sulfuric acid.

NOTE 2.—If the alloy contains molybdenum, the weighed tungstic oxide may contain a few hundredths of a per cent of molybdenum as MoO_3. If extreme accuracy is desired, the oxide should be tested colorimetrically. If the molybdenum content of the alloy is unknown, one of the sodium carbonate extracts of the impure WO_3 can be treated with tartaric and mineral acids and hydrogen sulfide and then if appreciable molybdenum is indicated, the amount should be determined in the sodium carbonate extract obtained in the duplicate run.

NOTE 3.—At the best, direct determination of tungsten in high-grade metal is subject to inherent errors. Accuracy within 0.2% is all that can be expected by any method.

METHOD FOR PHOSPHORUS IN TUNGSTEN METAL

Treat one gram of the finely powdered sample in a platinum dish, fitted with a gold cover, with 15 ml. HNO_3 (1.42 sp.gr.), add 3 ml. HF and warm gently. When action subsides, add 3 ml. more HF. After action subsides, boil, remove cover and if decomposition is not complete, add more HF and boil again. When solution is complete, wash off the cover and evaporate at a low heat to a volume of about 10 ml., then add 3–4 drops of concentrated permanganate solution and continue evaporation until crusts of WO_3 begin to form at the edges; that is, to a volume of about 6 ml. Add 5 ml. H_2SO_4 and evaporate on the stove at a low heat until HF and HNO_3 are expelled and H_2SO_4 fumes are given off. (Strong heat causes spattering and also causes hard, over-baked crusts to form on the bottom of the dish which resist subsequent treatment.) Cool, add 25 ml. H_2O and boil (by agitating over Bunsen flame) until all soluble salts are dissolved. Discharge pink color due to excess of permanganate by adding sulfurous acid drop by drop. The pink color may not be very evident but the SO_2 is added even so to reduce higher oxides of Mn. Boil for a minute or two after adding the SO_2. Add 1.2 grams of pure tartaric acid and when this is dissolved and the solution is cooled to a temperature of about 50° C., add 20 ml. of NH_4OH (0.90 sp.gr.) diluted with an equal volume of water. The precipitated tungstic acid should dissolve completely, giving a clear solution. The solution is hot from the reaction between H_2SO_4 and NH_4OH. While it is still hot add 2 g. of pure $MgSO_4$ dissolved in 10 ml. of water and transfer it from the Pt dish to a six-ounce glass stoppered

bottle. Set the bottle in ice water and when it has *thoroughly* cooled, add four or five glass beads of 6 mm. diameter. Stopper it tightly and shake in an efficient shaking machine for at least ten minutes. The agitation should be violent. The beads aid in starting the formation of the magnesium precipitate; after agitation add 15 ml. of concentrated NH_4OH and return the bottle to ice water tank and put it in a refrigerator to stand over night. Phosphorus separates as magnesium ammonium phosphate free from tungsten but containing possibly basic magnesium compounds. After standing over night, filter the solution through a 9-ml. paper containing a little paper pulp and wash the bottle and paper thoroughly by small additions of ammonia wash water (1 part NH_4OH, 3 parts H_2O). Do not attempt to remove all the precipitate from the bottle but remove the beads to the filter. The precipitate consists of magnesium ammonium phosphate and arsenate together with silica and other impurities. Tin, tungsten, molybdenum, vanadium and titanium are eliminated by precipitation with magnesium sulfate in the presence of tartaric acid. Dissolve the magnesia precipitate in hot dilute HCl and evaporate to a small volume, say 7 or 8 ml. Add 10 ml. of concentrated HCl and 0.5 g. of KBr and evaporate to dryness again. The KBr serves to reduce As^v to As'''. The addition of concentrated HCl and boiling followed by evaporation to dryness eliminates As. Dissolve residue in 60 ml. of HNO_3 (sp.gr. 1.135), filter into a 250-ml. shaking bottle; add 40 ml. of NH_4OH (sp.gr. 0.96), cool to 33° C., add 30 ml. of molybdate solution (Blair), and finish the determination by the alkalimetric method.

NOTE.—The usual proportions of HNO_3 and HF are reversed in order to provide a constant excess of HNO_3 to oxidize P. The procedure given takes a little longer than when the sample is treated with HF first and HNO_3 is added a little at a time, but solution is finally complete. It is necessary to keep the platinum dish covered after action begins, as the reaction is somewhat violent.

The platinum dishes recommended are:

8 cm. in diameter at top.
7.8 cm. in diameter at bottom.
4 cm. high.

They have flat bottoms and are wire-rimmed at top to give additional stiffness. They weigh 58 to 60 grams each and hold about 175 ml. The covers are made of pure gold (for economy) " dished " like a crucible cover to fit the top of the dishes closely. The dishes have small lips to aid pouring. The " tongue " of the cover overlaps the lip. Ordinary round bottomed dishes may be used but the manipulation is much more difficult; there is greater tendency to spattering and danger of local baking or overheating in evaporating to fumes of H_2SO_4. If the separated WO_3 is overheated locally it does not dissolve readily in NH_4OH. In a flat bottomed dish, the WO_3 is spread in a thin layer and heat is applied evenly all over the bottom.

A good shaking machine should be used. The magnesia precipitate may be started by shaking the bottles by hand, but it is a tiresome job. The solution must be cold—say 8° or 10° C. when shaking begins.

Permanganate solution is added to insure complete oxidation of phosphorus, as in steel analysis. The color of the permanganate gradually fades in the

hydrofluoric-nitric solution, but after evaporating to fumes and adding water, the solution is usually slightly pink.

The amount of tartaric acid is limited to 1.20 grams since ammonium tartrate retards the formation of the magnesia precipitate. Complete precipitation can only be obtained by brisk agitation and by keeping the solution very cold followed by long standing in a cold place. By this method, determinations started at 3 P.M. may be completed by noon of the next day.

Silicon

Fuse 0.9344 g. of the finely powdered metal, intimately mixed with 10 g. of dry Na_2O_2 in a 30-ml. pure iron crucible. The fusion is best made over a gas flame at a low temperature until the mass has melted down quietly, when the temperature is increased to approximately 900° C. for about 3 minutes. The crucible is given a rotary motion to stir up any unattacked particles of alloy adhering to the bottom or sides.

When the crucible has partly cooled, and with the cover (nickel) tightly on, it is tapped several times on an iron plate to loosen the fusion in a solid cake. Transfer the cake to a 300-ml. porcelain casserole of good glaze, cover and add 5 ml. of H_3PO_4 (sp.gr. 1.72), 80-ml. of H_2SO_4 (1 to 1) and 10 ml. of $HClO_4$, (60%). Rinse the crucible with a little hot water and add the rinsings to the casserole. Stir the solution well and boil gently until the temperature increases to 205° C. Continue the heating at this temperature for 5 minutes. A thermometer may be suspended just below the surface of the liquid in the lip of the casserole. At the temperature specified fumes of $HClO_4$ will be freely evolved.

The function of the phosphoric acid is to hold most of the tungsten in solution and to thus effect its separation from the silica.

Allow to cool somewhat and add 200 ml. of warm water. Heat until all ferric sulfate has dissolved, filter on an 11-cm. paper containing some ashless paper pulp and wash thoroughly (at least 20 times) with 1% H_2SO_4. Ignite in platinum first at a low temperature and finally at 1000° C., cool and weigh. Add several drops of H_2SO_4 and 1 or 2 ml. of HF and heat until fumes of SO_3 are no longer evolved. Heat the crucible for 5 minutes at 750° C., cool and weight. The loss in weight, corrected for any SiO_2 in the reagents and iron crucible, multiplied by 100 and divided by 2, gives the percentage of silicon in the alloy.

DETERMINATION OF SULFUR

Transfer 5 g. of the sample to a 300-ml. platinum dish provided with a platinum cover. Add 100 ml. of HNO_3 (sp.gr. 1.42) and add HF a few drops at a time, while heating, until the alloy has dissolved completely. Rinse and remove the cover. Add 1 g. of $NaNO_3$ and 30 ml. of $HClO_4$ (60%) and evaporate to strong fumes of $HClO_4$. Cool, rinse down with water, and again evaporate to fumes.

Add 100 ml. of water, 10 ml. of cinchonine solution (125 g. of cinchonine, sulfur-free, dissolved in 1 liter of 1 : 1 HCl) and some ashless paper pulp. Stir well, digest for 15 minutes at 60° to 70° C. and filter. Wash the tungstic acid with hot (2%) HCl containing 10 ml. of cinchonine solution per liter. Precipitate the sulfur as described on p. 908.

DETERMINATION OF COPPER, ANTIMONY AND TIN

Treat 5 g. of the 100-mesh sample in a 300-ml. platinum dish provided with a platinum or gold cover, with 50 ml. of HNO_3 (sp.gr. 1.42). Add HF (48%) a little at a time with occasional heating until the alloy is dissolved. Rinse the cover with water and evaporate to approximately 25 ml. Add 35 ml. of H_2SO_4 (sp.gr. 1.84) and continue the evaporation to dense fumes of sulfur trioxide. Allow to cool and transfer to a 600-ml. beaker. Rinse the dish successively with hot ammonia (1 : 1), 5 ml. of hot water, 5 ml. of hot H_2SO_4 (1 : 1) and finally with 10 ml. of hot water. Dilute with water to 400 ml., add 20 g. of tartaric acid and an excess (about 10 ml.) of ammonia and heat just short of boiling for several minutes. Add an excess of 2 ml. of H_2SO_4 (1 : 1) for each 100 ml. of solution and treat With a brisk stream of H_2S for at least 30 minutes Filter on an 11-cm. paper containing a little ashless paper pulp and wash thoroughly with 1% H_2SO_4 water containing 1% tartaric acid and saturated with H_2S.

(*a*) *Separation of Copper from Antimony Tin.*—Return the paper and sulfides to the beaker in which the precipitation was made and treat with 50 ml. of KOH–K_2S solution (prepared by saturating 1 volume of a 10% solution of KOH with H_2S and then adding 3 volumes of the solution). Add 1 g. of Na_2O_2 and heat to boiling in the course of 5 minutes and as the solution is occasionally stirred. Dilute with an equal volume of water, filter into a 400-ml. beaker and wash with a diluted K_2S solution (1 : 10). Reserve the filtrate (A).

(*b*) *Copper.*—Dissolve the residue and determine copper colorimetrically or electrolytically as described under Determination of Copper in Ferromolybdenum.

(*c*) *Separation of Tin and Antimony.*—Treat the reserve filtrate (*A*) with HCl until the solution is acid and then add 1 ml. per 100 ml. in excess. Filter, and wash with acidulated hydrogen sulfide water. Transfer the paper and sulfides to a 400-ml. beaker, treat with 10 ml. of HCl and add $KClO_3$, a few crystals at a time, as the solution is warmed to from 35 to 40° C. Dilute to 200 ml. and boil gently to expel chlorine. Add 5 g. of oxalic acid, heat to from 60 to 70° C. and pass in a rapid stream of H_2S for 20 to 30 minutes. Filter, and wash thoroughly with hydrogen sulfide water containing 0.5 ml. of sulfuric acid and a few crystals of oxalic acid per 100 ml. Reserve the filter paper and precipitate (*B*) for the determination of antimony.

(*d*) *Determination of Tin:*

Standard Solution of Iodine.—Dissolve 3.97 g. of iodine in a solution of 7 g. of KI in a little water. When solution is complete, dilute to 1 liter and mix thoroughly. One ml. of the solution should represent approximately 0.00185 g. of tin and the exact titer is found by dissolving 0.02 g. of pure tin in HCl, treating with lead as in the method, and titrating. For the small amounts of tin involved, the theoretical titer as based on standardization against pure arsenious oxide can be used.

Apparatus for Reduction of Tin.—The apparatus for reduction is shown in Fig. 126. At the point *A* a small hole about 1 mm. in diameter shall be blown in the glass. The glass rod *B* shall be drawn out at the end and covered with rubber tubing so as to form a light fitting stopper for the end of the tube *C*.

Treat the filtrate with 5 ml. of H_2SO_4 and evaporate to heavy fumes of the acid. Cool somewhat, and dilute with 100 ml. of water. Add 50 ml. of a solution of ferric sulfate (1%) and heat to boiling. Stir vigorously and add dilute NH_4OH (1 : 1) until the solution is alkaline and then add 3 to 5 ml. in excess. Let settle, filter, and wash with hot water. Dissolve the precipitate in 80 ml. of hot dilute HCl (1 : 1) and wash the filter with hot water, collecting the solution (not over 150 ml. in volume) in a 300-ml. Erlenmeyer flask. Add 1 to 2 g. of test lead and close the flask with a one-hole rubber stopper carrying a bent delivery tube, as shown in Fig. 126.

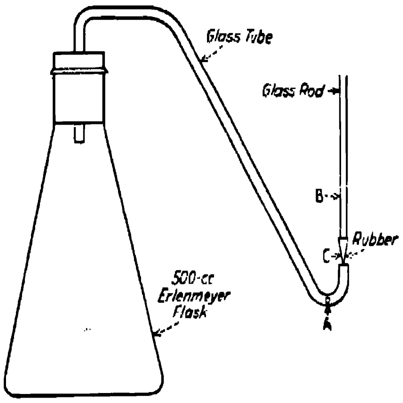


FIG. 126. Apparatus for Reduction of Tin.

Boil gently for 20 minutes. At the end of this period immerse the end of the delivery tube in a small beaker containing about 50 ml. of a strong solution of $NaHCO_3$ and insert the rubber-tipped tube at *C*, Fig. 126. Remove the flask and beaker from the hot plate and cool in a stream of cold water. When cool, remove the stopper, add 5 ml. of freshly prepared starch solution and titrate with the standard solution of iodine to a permanent blue tint. Subtract the volume required in a blank run and multiply by the tin titer of the solution.

(*e*) *Determination of Antimony.*—Spread the reserved filter paper and precipitate (*B*) side down, on a small watch glass and place this over a beaker containing a few centimeters of HCl and a drop or two of bromine. Warm the beaker until decomposition of the sulfide is complete. Rinse cover and paper with warm dilute HCl (1 : 9), keeping the volume down to 25 ml. Evaporate the solution to about 5 ml. on the steam bath and then add 1 g. of pure ferrous sulfate, 0.5 g. of potassium chloride, and 40 ml. of HCl. Evaporate the solution on the steam bath to a volume of about 5 ml. Dilute with 10 ml. of water, add 1 ml. of HNO_3 and heat until the iron is oxidized. Dilute to 100 ml. heat to boiling, and add dilute NH_4OH until in definite excess. Let settle, filter, and wash with warm water. Dissolve the precipitate in 10 to 15 ml. of hot dilute HCl (1 : 3) containing 0.1 g. of tartaric acid. Dilute to 100 ml., heat and add ammonium bisulfite drop-by-drop to reduce the iron. Boil to expel the excess of SO_2, cool and pass in a rapid stream of H_2S for 15 to 30 minutes. Filter through a weighed Gooch crucible and wash successively with acidulated hydrogen sulfide water, alcohol, ether and carbon disulfide. Heat in a radiator and add a *drop* of HNO_3, from time to time to oxidize the sulfide. Finally heat at about 600° C. and weigh as Sb_2O_4.

Determination of Tungsten in Steel.—See Volume II.

Acknowledgment is made to Mr. Thos. R. Cunningham, Chief Chemist of the Union Carbide and Carbon Research Laboratories, Inc., for the revision of this chapter.

URANIUM [1]

U, *at.wt.* 238.07; *sp.gr.* 18.7; *m.p.* <1850° C.; *oxides* UO_2, UO_3, (*oxide* U_3O_8, *formed by ignition* = UO_2+2UO_3)

The minerals of this comparatively rare element frequently occur in highly siliceous rocks, granite and sedimentary sandstones. It occurs in nature in the quadrivalent and sexivalent forms. It is found with the silicates, phosphates and zirconates of the rare earths and with columbium, tantalum and thorium. Pitchblende, an amorphous compound of uranium, occurs frequently with sulfide minerals. Rich deposits of pitchblende and modified forms occur in Belgian Congo. Other minerals of commercial importance are uraninite, a crystalline mineral varying in color from olive green, brown, gray to black, containing 40 to 90% U_3O_8 (i.e. $UO_2 \cdot 2UO_3$); frequently Ca, Th, Fe, Bi, Cu, Zn are present; carnotite, $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$, a mineral varying in color from canary yellow to red or black, commercial deposits in western Colorado and eastern Utah.

DETECTION

The mineral is warmed with a slight excess of nitric acid (1 : 1) until decomposition is complete. The solution is diluted with water and then an excess of sodium carbonate added and the mixture boiled and filtered. Sufficient nitric acid is added to neutralize the carbonate, and after expelling the CO_2 by boiling, sodium hydroxide is added to the filtrate. A yellow precipitate is formed in presence of uranium. The precipitate is insoluble in an excess of the reagent, but dissolves in ammonium carbonate.

Uranous salts are green or blue and form green or bluish-green solutions, from which alkalies precipitate uranous hydroxide, reddish brown, insoluble in excess, but readily dissolved by ammonium carbonate. Uranous salts are strong reducing agents.

Uranyl salts ($UO_2 \cdot R_2$) are yellow. Alkali carbonates give a yellow precipitate, soluble in excess. UO_2^{++} is regarded as a basic radical, known as "uranyl." The radical migrates to the cathode, upon electrolysis of a uranyl solution. Uranyl salts are more stable than uranous and are better known.

Potassium ferrocyanide, $K_4Fe(CN)_6$, added to uranous or uranyl solutions gives a reddish brown precipitate (or a red color in dilute solutions). The

[1] The element was discovered by Klaproth in 1789 in uraninite and carnotite. Uses for the metal have not been developed. Sodium uranate is used in coloring pottery. Uranium and its salts are radioactive.

precipitate dissolves in a large excess of HCl. If sufficient ferrocyanide is present the color changes to green on boiling. Addition of sodium hydroxide to the ferrocyanide precipitate of uranium changes the color to yellow. (Distinction from cupric ferrocyanide. Ferrocyanide gives a green precipitate with vanadium, the color deepens on addition of nitric acid. A blue color is produced with ferric iron. No color change with chromates. Distinction from vanadium, chromium and iron.)

Barium carbonate precipitates the uranic ion completely (distinction from the ions of nickel, cobalt, manganese, zinc).

Disodium hydrogen phosphate added to uranyl solutions in presence of alkali acetates or free acetic acid gives a yellowish white precipitate, $UO_2HPO_4 \cdot xH_2O$, soluble in mineral acids. Warming promotes precipitation.

Tartaric acid, certain organic compounds, hydroxylamine hydrochloride, ammonium carbonate, prevent precipitation of uranium by alkalies and ammonia.

Oxides UO_2, brown or black; UO_3, brick red; $UO_2(OH)_2$, yellow. All oxides are converted to U_3O_8 on ignition with free access of air.

ESTIMATION

Both gravimetric and volumetric procedures are employed in the estimation of uranium. Owing to the difficulty of completely removing nitric acid, whose presence interferes in the volumetric procedures, this acid is not employed for decomposition, when followed by volumetric reduction and titration,[2] unless especial precautions are used in its removal. It does not interfere in gravimetric determinations.

Uranium is used in ceramic industry for producing green, yellow, brown, gray or velvety-black tints. It produces canary yellow in glass. It is used as a mordant in dyeing silk and wool. It is used in photography, and as a metal in cigarette-lighters and self-lighting burners.

In analytical procedures, in absence of CO_2 and V, uranium precipitates with addition of ammonia and unless accounted for will cause an error in the iron and aluminum determinations, in the determination of aluminum if SO_2, H_2S or $SnCl_2$ is used for reducing Fe (these do not reduce uranium) or in the iron determination if Zn is used in the reduction (uranium also reduced).

The presence of CO_2 prevents precipitation of uranium. Advantage may be taken of this in separating uranium from elements precipitated by ammonium hydroxide.

The minerals are easily decomposed by acids. The method of decomposition depends largely on the later procedure for estimation. Details will be considered in later sections of the chapter.

[2] J. A. Holladay and T. R. Cunningham, Trans. Am. Electrochem. Soc., **43**, 329 (1923).

PREPARATION AND SOLUTION OF THE SAMPLE

The element dissolves in hydrochloric and in sulfuric acids; less readily in nitric acid. It is insoluble in alkaline solutions.

The oxide, UO_2, dissolves in nitric acid and in concentrated sulfuric acid.

U_3O_8 is readily soluble in nitric acid, but dissolves with difficulty in hydrochloric acid. V_2O_5 dissolves with difficulty in nitric acid but easily in hydrochloric (red colored solution); U_3O_8 is readily soluble in a mixture of glacial acetic-nitric acids (100 : 5); V_2O_5 and Fe_2O_3 (ignited) are practically insoluble in this reagent.

The salts, UF_4 and $UO_2(HPO_4)_2 \cdot 4H_2O$, are insoluble in water, but dissolve in strong mineral acids.

Solution of Ores.—One gram or more of the ore is dissolved with 15 to 20 ml. of aqua regia, by placing the mixture first on the steam bath for ten to fifteen minutes and then gently boiling over a low flame or on the hot plate. The solution is taken to dryness, silica dehydrated as usual, the residue treated with 10 ml. of hot dilute hydrochloric acid and diluted to about 50 ml. with hot water and the silica filtered off. Uranium passes into the filtrate. The solution is now treated as directed under Separations. If much silica or acid-insoluble matter is present, this should be treated in a platinum dish with concentrated hydrofluoric acid, and evaporated twice on the steam bath with hydrochloric acid to expel HF. The residue, dissolved with hydrochloric acid and water, is added to the first portion of solution obtained.

Carnotite.—Solution of the ore is readily effected by boiling with nitric acid to which a little hydrofluoric acid is added. One gram of ore with 20 ml. nitric acid and 5 ml. hydrofluoric acid at boiling temperature will be completely decomposed in five minutes. Some authorities recommend addition of sulfuric acid with ores containing barium to break up the combination of barium and uranium. If the lead acetate separation of vanadium is used, the sulfuric acid should be expelled previously to this separation. Consult the gravimetric procedures following the section on "Separations."

Decomposition Preparatory to Volumetric Procedure.—The ore is decomposed by sulfuric acid. If titano-columbates and other highly refractory substances are present, fusion with sodium pyrosulfate followed by sulfuric acid is recommended, or sulfuric and hydrofluoric acids, with subsequent expulsion of HF. Ores high in silicates are best decomposed by action of HF with HCl or H_2SO_4.

SEPARATIONS

Separation of Uranium from Copper, Lead, Bismuth, Arsenic, Antimony and the Other Members of the Hydrogen Sulfide Group.—The solution containing uranium, etc., having an acidity of about 5 ml. concentrated HCl per 100 ml. of solution, is saturated with hydrogen sulfide and allowed to settle

and again saturated with H_2S. The sulfides are filtered off and washed. The filtrate and washings contain the uranium that was present in the sample.

Separation of Uranium from Iron and from Elements Having Water-insoluble Carbonates.—The filtrate from the hydrogen sulfide group is concentrated to about 150 ml., and 15 ml. of hydrogen peroxide added. The solution is now neutralized with sodium carbonate and about 3 grams added in excess. After boiling for about twenty minutes, renewing the water evaporated, the hydroxide of iron, insoluble carbonates, etc., are filtered off, washed with hot water and the filtrate set aside for the determination of uranium. To recover any occluded uranium the precipitate is dissolved in just sufficient nitric acid to effect solution, and iron again precipitated by addition of hydrogen peroxide and sodium carbonate and boiling as directed above. The combined filtrates from this precipitate are concentrated to about 250 ml. Iron may also be removed by extraction with ether. See Separation in the chapter on Iron.

Separation of Uranium from Vanadium. Procedure 1. ***To be Used in the Gravimetric Determination of Uranium.***—The solution obtained as directed, under the previous separation, is acidified with nitric acid, adding a slight excess, and CO_2 expelled by boiling 20–30 minutes, or by evaporation nearly to dryness. The acid is now neutralized with ammonia in slight excess, then re-acidified with nitric acid in slight excess, finally adding about 4 ml. of the concentrated acid additional. Vanadium is now precipitated as lead vanadate by adding 10 ml. of a 10% solution of lead acetate, followed by sufficient strong ammonium acetate solution (1 vol. concentrated NH_4OH+1 vol. H_2O+sufficient glacial acetic acid to neutralize the NH_4OH) to neutralize the free nitric acid (about 20 ml.). The precipitated lead vanadate is allowed to settle for a couple of hours on the steam bath, and is then filtered off (returning the first portions if not perfectly clear) and washed well with hot water. The uranium passes into the filtrate.

The excess of lead remaining in the filtrate is next removed. A marked excess of ammonia is added to the hot filtrate, which is then boiled for about a minute and filtered. No washing required. The precipitate contains all the uranium as ammonium uranate, perhaps some ferric and aluminum hydroxides and a portion of the lead. Most of the lead passes into the filtrate, which is discarded. The precipitate is now treated on the filter with a strong hot solution of ammonium carbonate containing a little free ammonia until all the uranium is dissolved and then washed with the same solution diluted. Most of the admixed lead and other impurities remain on the filter, the lead as carbonate. Sufficient strong hydrogen sulfide water is now added to the filtrate, or the gas is passed to precipitate all the lead remaining. The mixture is heated to boiling and then allowed to stand until clear. Any iron present is precipitated with the lead. Finally, the uranium solution is filtered off and the precipitate washed with hydrogen sulfide water containing a little ammonium carbonate. The filtrate is boiled to expel the hydrogen sulfide and ammonium carbonate and concentrated to 200–250 ml. Uranium is now precipitated and determined by the gravimetric procedure given on page 1022.

Procedure 2. ***To be Used in the Volumetric Determination of Uranium.***—The separation of vanadium from uranium may be effected by precipitation of the latter as a phosphate according to the following procedure. The solution

is heated and allowed to run in a small stream through a funnel with constricted stem, into a boiling solution of 15 grams of ammonium acetate, 5 grams of microcosmic salt dissolved in 100 ml. of water containing about 5 ml. of glacial acetic acid. A rod, with a cup-shaped tip, placed in the solution prevents bumping. The mixture is allowed to boil for a few minutes, the beaker is then removed from the heat and the precipitate allowed to settle. This is now transferred to a filter after first decanting off the clear solution. It is washed once with hot water, then washed back into the beaker and dissolved in a small amount of hot dilute nitric acid, the precipitate clinging to the filter being dissolved off by the acid, which is allowed to run through the filter into the beaker. This nitric acid solution containing the vanadium is diluted to about 75 ml. and the uranium (together with aluminum if present) again precipitated as the phosphate according to the procedure described. The precipitate is again transferred to the filter previously used, and washed off with hot water four or five times. Vanadium passes into the filtrate. The phosphate is now dissolved off the filter with 15 ml. of hot dilute sulfuric acid (1 : 3), and uranium determined by titration with permanganate according to the directions given under the volumetric method described later.

Glacial Acetic Method for Separating Uranium from Vanadium.[3]—Uranium nitrate or oxide dissolves readily in a mixture of glacial acetic acid and nitric acid, 20 parts of the former to 1 part of the latter. The nitrate and oxide of vanadium are insoluble in the reagent. Addition of water causes vanadium to dissolve. See method for determining uranium in Carnotite under the "Gravimetric" methods.

Separation of Uranium from Molybdenum, Tungsten and Vanadium.[3]—The residue obtained by evaporating a mixture of uranyl nitrate and nitric acid with ammonium molybdate, or sodium tungstate, or sodium vanadate to dryness, is slightly moistened with nitric acid (5 ml. HNO_3 sp. gr. 1.42) and extracted with ether; uranium dissolves completely while molybdenum, tungsten and vanadium remain insoluble. The evaporation is conveniently conducted in a glass boat of a size that may be placed in the paper thimble of a Soxhlet extraction apparatus, commonly used with volatile solvents. The extraction is generally complete after the ether has siphoned over five or six times.

Separations by Cupferron.—Sexivalent uranium is not precipitated by cupferron; this enables a separation of UO_3 from Fe, Ti, V and Zr. The solution containing about 10% of its volume of H_2SO_4 is oxidized by addition of $KMnO_4$ reagent to a faint pink and then a 6% water solution of cupferron in excess. Stir in macerated filter paper, filter and wash with 10% HCl or H_2SO_4 solution containing 0.2 g. cupferron per 100 ml. Uranium passes into the filtrate.

Precipitation of Uranium.—A little HNO_3 is added and the solution evaporated to H_2SO_4 fumes to destroy organic matter (cupferron, etc.). The residue is taken up with water and diluted so as to contain about 6 ml. H_2SO_4 per 100 ml. and the uranium reduced by passing through a column of zinc exactly as in case of iron reduction. Uranium is now precipitated from the reduced solution by addition of the cupferron reagent. Al, Cr, Mn and P

[3] Peligot, Ann. chim. phys. (3), 5 (1842). C. A. Pierlé, J. Ind. Eng. Chem., 21, 60 (1920).

remain in solution. The precipitate is washed with dilute H_2SO_4 (2 ml. H_2SO_4 per 100 ml.) containing a small amount of cupferron (0.2 g. per 100 ml.), and ignited to U_3O_8.

Sexivalent uranium forms a soluble fluoride, quadrivalent uranium fluoride is insoluble. This enables a separation of the two forms.

The presence of ammonium carbonate prevents precipitation of uranium either by NH_4OH or $(NH_4)_2S$; facts that enable separations of uranium from Fe, Al, Co, Ni, Zn, Ti, etc. Tartrates also prevent precipitation of uranium. If sodium or potassium carbonates are used the addition of sodium peroxide is recommended as improving the separations.

GRAVIMETRIC DETERMINATION OF URANIUM AS THE OXIDE, U_3O_8

Procedure.—The filtrate containing the uranium, as obtained according to the method given under "Separations," is made slightly acid with nitric acid and boiled for a short time to ensure the absence of CO_2, then ammonia is added in marked excess, the mixture boiled for about a minute more and filtered. No washing necessary. Either paper or a weighed Gooch crucible may be used for the filtration. The precipitate is dried and ignited to the oxide U_3O_8, in which form it is weighed.

$$U_3O_8 \times 0.8480 = U.$$

NOTES.—The purity of the oxide may be ascertained by dissolving in HNO_3 and testing for vanadium with H_2O_2 and for Al_2O_3 by adding $(NH_4)_2CO_3$.

Treadwell recommends that the oxide be reduced by hydrogen passed over the red-hot residue, the brown UO_2 being formed. The oxide is cooled in a current of hydrogen.

GRAVIMETRIC METHOD FOR URANIUM IN ORES [4]

Take 0.5 gram of the finely ground ore, or more, according to richness. Treat by heating gently in an 8-oz. "copper flask" with nitric or hydrochloric acid, or both, together with about 1–2 ml. of hydrofluoric acid, to effect complete solution of the uranium. Sometimes galena is present, in which case it is best to start with 10 ml. or more of hydrochloric acid and heat until the galena is decomposed. Whenever hydrochloric acid is used, boil almost to dryness to

[4] By Albert H. Low.

expel most of it before continuing. To this residue, or to the original ore, if hydrochloric acid appeared unnecessary, add 10 ml. of nitric acid and 1–2 ml. of hydrofluoric acid. Boil very gently to effect complete decomposition, and finally to approximate dryness. Allow to cool, add 3 ml. of nitric acid and 50 ml. of hot water, and see that everything soluble is dissolved.

Now make slightly alkaline with ammonia, then just acid with nitric acid, and again alkaline with a little solid ammonium carbonate, followed by about 5 ml. of concentrated ammonia and 3–4 grams more of ammonium carbonate.

Boil for about a minute and then filter, having a wetted wad of absorbent cotton in the apex of the filter. Wash twice with hot water. Boil and concentrate the filtrate in a covered beaker during the next step.

Dissolve the precipitate on the filter with a little hot dilute nitric acid, receiving the filtrate in the original flask. Again neutralize and precipitate as before, washing this second precipitate well with hot water. Add the filtrate to the first one and continue the concentration to 150–200 ml. Now acidify with nitric acid, and then, in case of doubt, add about 1 ml. of hydrogen peroxide. A reddish brown color indicates vanadium.

A. *Vanadium Present.*—Boil to expel any remaining CO_2, make just alkaline with ammonia, then just acid with nitric acid, finally adding about 4 ml. of the latter in excess. The appearance of the liquid is usually a sufficient indication of the neutralization points. Now add 1 gram of lead acetate crystals and then sufficient ammonium acetate solution (about 20 ml.) to neutralize the nitric acid and precipitate the lead vanadate. Boil for about 10 minutes and then filter through a double filter, returning the first portions if not perfectly clear. Wash with hot water. Receive the filtrate in a large beaker. If bulky, boil down to perhaps 200–250 ml. Now add ammonia in marked excess and boil for a minute to expel any CO_2. Filter hot, paying no attention to a turbid filtrate unless it is yellowish (in which case wash the precipitate once with hot water, re-acidify the filtrate with nitric acid, heat to boiling and again precipitate with ammonia, filtering through the previous precipitate). No washing required. Place the last beaker under the funnel and fill the latter with a strong hot solution of ammonium carbonate, to which some free ammonia has been added. Usually one filling is sufficient to dissolve all the uranium and leave a white residue of lead carbonate, perhaps slightly discolored by a trace of iron. Wash with hot water, using a little more of the ammonium carbonate solution, if apparently necessary. Add to the filtrate sufficient strong hydrogen sulfide water to precipitate all the remaining lead (ordinarily 25 ml. of strong hydrogen sulfide water), or pass the gas for a short time. This also removes traces of iron. Heat to boiling, then allow to stand and settle. Filter, washing with hydrogen sulfide water containing some ammonium carbonate. Boil to expel the sulfide, then acidify with nitric acid and boil off all CO_2. Continue according to C.

B. *Vanadium Absent.*—Boil the nitric acid solution sufficiently to expel all CO_2, then add ammonia in marked excess and boil a little longer to expel any CO_2 in the ammonia. Filter the hot mixture, returning the first portions if not perfectly clear. No washing required. Dissolve the uranium on the filter with hot ammonium carbonate solution, as described in the last paragraph, and continue from this point as in the same situation above. Do not

omit the hydrogen sulfide treatment, for, even in the absence of lead, there will usually be traces of iron to be removed. Continue according to C.

C. Add ammonia in marked excess, boil well for one minute and then filter through an ashless filter, returning the first portions if not clear. No washing required. Ignite filter and precipitate thoroughly in a porcelain crucible and weigh, after cooling, as U_3O_8. Impurities are usually present.

Dissolve the residue in the crucible by warming with a little nitric acid. Dilute and test for vanadium with hydrogen peroxide. A faint brownish tinge may be neglected. Rinse the solution into a small beaker, add solid ammonium carbonate in excess, boil a minute or two and then filter through a small filter, washing with hot water. The residue on the filter may consist of alumina and other insoluble matter. Ignite filter and residue in the original crucible, weigh and deduct the weight from that of the impure U_3O_8 previously found.

Ammonium Acetate Solution.—Eighty milliliters of concentrated ammonia, 100 ml. of water and 70 ml. of 90% glacial acetic acid.

NOTE.—A yellow filtrate from the ammonium uranate indicates incomplete precipitation. This may be due to a deficiency in ammonium nitrate, as ammonium uranate is perceptibly soluble in pure water. Add a gram or so of ammonium nitrate to the filtrate, boil and refilter. Or, better, dissolve the precipitate on the filter with dilute nitric acid, so that the mixed filtrates will be markedly acid, and repeat the precipitation with ammonia. The filtrate should be colorless.

Precipitation of Uranium with Ammonium Hydroxide.—In absence of other elements precipitated by NH_4OH and in absence of vanadium and carbon dioxide (which prevents precipitation) uranium may be precipitated by addition of NH_4OH, the precipitate washed with 60 ml. NH_4NO_3 solution and ignited to U_3O_8.

The procedure necessitates separation of Fe, Al, Ti, etc., elements precipitated by NH_4OH, and complete removal of CO_2. PO_4 must be absent, as well as organic matter.

GLACIAL ACETIC ACID METHOD FOR DETERMINING URANIUM IN CARNOTITE[5]

The following method depends upon the fact that uranium nitrate or oxide is soluble in a mixture of glacial acetic and nitric acids in the proportion of 20 parts by volume of the former to 1 part of the latter, while vanadic nitrate and oxide (V_2O_5) are not.[6]

Procedure.—Half a gram or more of carnotite ore according to its richness (ground to pass 100-mesh sieve) is taken for analysis and digested at boiling temperature with 25 ml. dilute HNO_3 (1 : 1) and 1–2 ml. HF. (An amount that will fill a small crucible lid.) The solution is rapidly evaporated to dryness and baked gently to expel water, but not ignited.

[5] Wilfred W. Scott, J. Ind. Eng. Chem., 14, 531 (1922).
[6] C. A. Pierlé, J. Ind. Eng. Chem., 12, 61 (1920).

Fifteen to 20 ml. of glacial acetic-nitric reagent (20 : 1) are added, rinsing down the sides of the beaker to remove any adhering material, using a policeman if necessary. (The reagent may be conveniently handled in a small wash bottle, the transferring of precipitates and washing with the reagent being necessary, no water being used at this stage.) The residue transferred to a filter is washed with the reagent five or six times, using small portions of the mixture.

The filtrate and glacial washings are rapidly evaporated to dryness and the residue again extracted with glacial acetic nitric acids.[7] This extract, free from vanadium,[8] is evaporated to dryness, and gently heated over a free flame until the residue turns dark.[9] Ten ml. of nitric acid and 40 ml. of water are added and the mixture heated to dissolve the uranium.

The greater part of the free nitric acid is neutralized by addition of ammonia (no permanent precipitate should form). Solid ammonium carbonate is added (covering the beaker during the intervals between additions of the carbonate as loss will occur through effervescence in an uncovered beaker) until a precipitate forms that remains undissolved on stirring. Two to 3 grams additional ammonium carbonate and 5 ml. of ammonium hydroxide are now added and the solution warmed to coagulate the hydroxides of iron and aluminum. Uranium passes into solution.

The precipitate is filtered off and washed with hot water. The filtrate and washings (concentrated by boiling to about 150 ml.–200 ml. if the volume is large) is acidified with nitric acid (uranium precipitates and redissolves).[10] Carbon dioxide is expelled by boiling and a decided excess of ammonium hydroxide added. The boiling is now continued until uranium precipitates completely. If the supernatant solution is yellow, it is again acidified with nitric acid, followed by an excess of ammonium hydroxide and the boiling repeated This generally effects complete precipitation in about 30 minutes.[11]

The precipitated uranium is filtered off, washing being unnecessary. The filter and precipitate are placed in a crucible, the greater part of the water expelled by drying and the material then ignited. The greenish black residue is weighed as U_3O_8.

[7] Uranium dissolves completely in the glacial-acetic mixture. A small amount of the vanadium may dissolve, hence the extract is evaporated and the residue again extracted. A smaller quantity of the reagent may be used in this second extraction. Twenty-five ml. of the reagent will dissolve, at boiling temperature, about 4.5 grams of U_3O_8 in five minutes and about 0.003 gram of V_2O_5. The proportion of glacial acetic acid to nitric acid should not fall below 10 : 1, otherwise vanadium will dissolve in appreciable amount. The author uses a round bottom flask filled with cold water, placing this over the beaker to act as a condenser to prevent loss of acetic acid.

[8] The acetic acid extract filters rapidly. The red colored residue contains the vanadium and practically all of the silica, iron and alumina.

[9] The residue is ignited to destroy organic matter which would prevent precipitation of uranium by ammonia.

[10] Uranium carbonate precipitates and then dissolves in the acid when present in excess. CO_2 must be expelled as this prevents precipitation of uranium by ammonium hydroxide.

[11] A colored solution indicates the presence of uranium. The nitrate formed by acidification with HNO_3 and making alkaline with ammonia with additional boiling insures complete precipitation of uranium. If desired the solution may be taken to near dryness to insure expulsion of CO_2.

This residue should be soluble when boiled with nitric acid.[12] If it is not, contamination by iron and aluminum is indicated. Any residue remaining should be filtered off, then washed free of uranium with hot water, and ignited. Its weight is subtracted from the uranium oxide to obtain the true value of U_3O_8.

DETERMINATION OF URANIUM IN CARNOTITE

The following method, worked out by C. E. Scholl,[13] is adapted for eliminating the difficulties in an accurate determination of uranium, caused by the presence of iron, alumina and vanadium, which commonly occur in carnotite.

Procedure.—To the sample of material containing about 0.2 gram uranium oxide, are added 25 to 50 ml. 1 : 1 nitric acid and heat applied until all the uranium is in solution. If necessary, allow to stand on the water bath to keep warm over-night. After diluting with warm water to 250 ml. the solution is filtered. Ferric chloride, equivalent to about three times the weight of vanadium present, is added. To the cold or slightly warm solution solid sodium carbonate is now added in small portions until all the acid is neutralized and then an excess of 1 gram added, the beaker being kept covered during the intervals between the additions. The sample is placed on a hot plate and heated to about 90° C., but not to boiling. After keeping hot for 15 minutes, the solution is filtered and washed. The residue contains all the iron and vanadium and the greater part of the aluminum. The filtrate is neutralized cautiously with nitric acid until uranium begins to precipitate. The greater part of the CO_2 is removed by boiling. Sodium hydroxide is now added in excess and after boiling 15 minutes the solution is filtered. The filtrate contains the remainder of the aluminum and the vanadium not previously precipitated. The precipitate containing the uranium is dissolved in dilute nitric acid and heated to 90° C. and an excess of NH_4OH added and the solution boiled. The precipitate is filtered off, ignited and weighed as uranium oxide, U_3O_8.

The oxide is tested for its purity with nitric acid as in the previous method.

Cupferron Method.—Quadrivalent uranium is precipitated by cupferron after removal of elements also precipitated by this reagent. See Separations.

[12] Nitric acid dissolves uranium oxide very easily. The oxide of iron is practically insoluble. Vanadic oxide difficulty soluble.

Hydrogen peroxide added to the nitric extract will produce a reddish brown color if vanadium is present.

Wash water used in transferring the uranium precipitate should contain ammonium nitrate to prevent solution of uranium.

[13] Jour. Ind. Eng. Chem., Vol. 11, No. 9, p. 842, Sept., 1919.

VOLUMETRIC DETERMINATION OF URANIUM BY REDUCTION AND OXIDATION

Introduction.—The determination of uranium by oxidation of the lower oxide UO_2 to UO_3 may be accomplished by means of potassium permanganate in precisely the same manner as in the determination of iron, the Jones reductor being used for the reduction of the uranic salt to the uranous form. The metal must be in solution either as a sulfate, a chloride or an acetate, but not as a nitrate. If present as a chloride the usual preventative solution of phosphoric acid and manganous sulfate solution must be present as in case of the titration of a chloride of iron, hence a sulfate solution is to be preferred. Although the degree of reduction varies with conditions, it is found that with brief contact with the oxygen of the air the oxide UO_2 is formed.[14]

Solution.—The ore is preferably dissolved in sulfuric acid or by fusion with sodium pyrosulfate followed by sulfuric acid. Elements reduced by zinc and subsequently titrated by permanganate must be removed (Fe, Ti, Mo, V, HNO_3, etc.). Carbon dioxide must be expelled in separations by means of ammonium carbonate or sodium or potassium carbonates by acidifying with H_2SO_4 and boiling. The uranium sulfate solution, diluted to a volume of 100 to 150 ml., containing one-twentieth of its volume of sulfuric acid, is heated nearly to boiling and the organic matter that may be present oxidized by addition of just sufficient potassium permanganate solution to produce a faint pink color. The solution is now cooled and is ready for reduction. Fifteen to 20 ml. of dilute sulfuric acid are passed through the 18-in. column of amalgamated zinc in the Jones reductor, followed by the uranium sulfate solution drawn through slowly. The uranic solution is followed by 10 to 15 ml. of dilute 1 : 20 solution of sulfuric acid.

Titration.—The olive-green solution is poured into a beaker or casserole and stirred with a rapid stream of air for 5 minutes.[15] The lower oxides are oxidized to UO_2 by the air, as seen by the slight change of color to sea green. The solution is now titrated with tenth normal permanganate. The solution during titration gradually becomes more and more yellowish green, as the highest oxidation is approached, until a faint pink color is obtained. With large amounts of uranium the color appears a yellowish pink.

$$\text{One milliliter N/10 } KMnO_4 = 0.01190 \text{ gram U.}$$

Note.—55.84 grams Fe is equivalent to 119.04 grams U.

A blank should be run on the reagents used by passing the exact volumes through the reductor and titrating with the permanganate reagent. This blank must be deducted from the titration of the uranium.

[14] Oxidation of lower oxides by air to UO_2. O. S. Pulman, Jr. Am. J. Sci. (4), 16, 229. Uranium is not reduced to UO_2 by passage of hot or boiling H_2SO_4 solution through a zinc reductor. To effect this reduction the temperature of the solution should not exceed 25° C.

[15] Lundell and Knowles, J. Ind. Eng. Chem., 16, 723 (1924); J. Am. Chem. Soc., 47, 2637 (1925). The U^{IV} may also be titrated with ceric sulfate as proved by Furman and Schoonover, J. Am. Chem. Soc., 53, 2561 (1931), or with potassium bichromate according to Kolthoff and Lingane, J. Am. Chem. Soc., 55, 1871 (1933).

DETERMINATION OF URANIUM IN ALLOY STEELS AND FERRO-URANIUM[16]

The following method provides for the analysis of steels containing Cr, Mo, V, W, Co, Ni, C, Mn, Si, Al and Ti.

A 2 g. sample is dissolved in 75 ml. of 1 : 1 hydrochloric acid. After solution is complete the solution is oxidized by the dropwise addition of nitric acid. In the case of samples where tungsten is present an easily filterable product is obtained by diluting to 300 ml. and boiling for 15 minutes. The tungstic oxide is then filtered out and washed, the filtrate and wash waters being returned to the original beaker for evaporation to dryness, followed by baking at a moderate temperature. On dissolving the residue with 50 ml. of 1 : 1 hydrochloric acid and diluting with hot water, a solution is obtained from which the balance of the silica and the last traces of tungsten can be separated by filtering. The two precipitates after washing are available for the determination of tungsten and silicon by the usual methods. Filtrates and wash waters from these precipitates are combined and evaporated to a syrupy consistency in preparation for the extraction of most of the iron with ether. In the absence of tungsten the original solution is evaporated to dryness and baked with the object of removing silica. After the extraction of the iron, the aqueous layer is evaporated to a small volume to free it from the excess of acid. It is then diluted to a volume of 150 ml. with hot water, and an excess of sodium carbonate in the form of a saturated solution is added. This solution is boiled and, after settling, filtered, the precipitate being washed with hot water. The precipitate consists of the hydroxides of chromium, iron, manganese, cobalt, nickel, copper, and aluminum, if all of these elements are present, together with traces of silica, titanic oxide, phosphorus, and vanadium compounds. The filtrate contains uranium, molybdenum, vanadium, and traces of the elements which occur chiefly in the precipitates.

Bulky precipitates should be dissolved in hydrochloric acid and reprecipitated one or more times with sodium carbonate solution to insure a complete separation of the uranium.

All filtrates from the precipitate are cautiously acidified with sulfuric acid and boiled long enough to insure the complete removal of all carbon dioxide. Ammonia free from carbonate is then added in slight excess. Boiling precipitates the uranium, much of the vanadium, and traces of impurities. The molybdenum is left in the filtrate. Steels contain only small amounts of phosphorus and the contamination of the uranium from this source is usually negligible. If the amount of phosphorus is large, it may be necessary to dissolve the precipitate in nitric acid, and after suitable oxidation, precipitate the phosphoric acid with ammonium molybdate. The phosphorus can then be removed as ammonium phosphomolybdate. The uranium and vanadium may be reprecipitated from this filtrate along with the manganese, if permanganate is used to oxidize the phosphorus, by adding a few drops of sulfuric acid, a small amount of ammonium persulfate, and enough carbonate-free ammonium hydroxide to give an excess. The precipitate obtained by boiling the solution is in the condition corresponding to the first uranium precipitate mentioned above.

[16] By G. L. Kelley, F. B. Myers and C. B. Illingworth, J. Ind. Eng. Chem., 11, 316 (1919).

The impure uranium precipitate containing phosphorus in negligible amounts, or free from it, is transferred to a beaker with a little water and solid ammonium carbonate added. On heating this solution under conditions and for a time calculated to result in only a partial decomposition of the ammonium carbonate, the uranium and vanadium go into solution leaving the manganese, iron, and other impurities undissolved. The filtrate is acidified with sulfuric acid and boiled until free from CO_2, when a slight excess of carbonate-free ammonium hydroxide is added. This precipitates only the uranium and vanadium.

The combined precipitates of uranium and vanadium are ignited at dull redness in a platinum crucible, allowing free access of air to reoxidize any reduced material. The ignited residue is weighed as $U_3O_8+V_2O_5$. In general, only a small part of the vanadium is present in this precipitate, thus making it unavailable for the vanadium determination. It is necessary, however, to determine the vanadium to correct the weight of uranium oxide. This may be done by almost any of the several known methods for determining vanadium. To this end we determine the vanadium after reduction with hydrochloric acid by permanganate titration, and by oxidation with ammonium persulfate and silver nitrate, followed by electrometric titration. The latter method is the more certain and convenient, but the former gives entirely satisfactory results. For the purpose of either method the precipitate is dissolved in 50 ml. of concentrated hydrochloric acid and evaporated with 30 ml. of sulfuric acid (sp.gr. 1.58) until fumes appear. When the titration is to be completed with permanganate, the sulfuric acid solution is diluted to 250 ml. with hot water and titrated at 80° C. to the first pink color. At the same time like quantities of sulfuric and hydrochloric acids are evaporated, diluted, and titrated in similar fashion to obtain a blank correction for the vanadium. When the titration is to be made electrometrically, the sulfuric acid solution is diluted to 250 ml. with hot water, oxidized with silver nitrate and ammonium persulfate and titrated with ferrous sulfate. The weight of vanadium so found is multiplied by 1.784 to convert it into the corresponding weight of the oxide V_2O_5. This weight is subtracted from the weight of the residue $U_3O_8+V_2O_5$. The corrected weight of the oxide U_3O_8 is converted into the corresponding weight of uranium by multiplying by 0.8481 from which the percentage of uranium can be calculated.

Uranium and Vanadium in Ores. See Chapter on Vanadium.

VANADIUM[1]

V, *at.wt.* 50.95; *sp.gr.* 6.025; *m.p.* 1720° C.; *oxides* V_2O, V_2O_2, V_2O_3, V_2O_4, V_2O_5; *vanadates—meta* $NaVO_3$, *ortho* Na_3VO_4, *pyro* $Na_4V_2O_7$, *tetra* $Na_3HV_6O_{17}$, *hexa* $Na_2H_2V_6O_{17}$

Vanadium is widely distributed in nature in ores, clays, hard coal, igneous rocks, limestones, sandstones; but not in appreciable amounts in high silicious rocks. It occurs in ores of copper and lead, in basalts, in soda ash, phosphate soda, blast furnace slags. The following are the more important vanadium minerals: vanadinite, $(PbCl)Pb_4(VO_4)_3$, (8–21% V_2O_5), associated with lead ores, a deep red, yellow or brown mineral, with white to pale yellow streak; patronite, the principal source of vanadium, a sulfide of vanadium (28–34% V_2O_5), associated with pyrites and carbonaceous matter, greenish-black, resembling slaty coal; roscoelite, a vanadium mica with variable composition, dark green to brown; carnotite, $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$ (19–20% V_2O_5); other minerals in which vanadium is associated with lead, zinc, copper, aluminum, manganese, bismuth calcium and barium.

Vanadium is used in production of many special steels. Tool steels also very frequently contain vanadium either alone or in combination with other elements, the amounts ranging from .20 to 1.00%. All American high speed tool steels contain vanadium associated with tungsten and chromium and sometimes other elements; in these products the proportions are generally from .75 to 2.50%.

In the chemical industries vanadium compounds have been used in indelible inks, in the mordanting of aniline black on silk, in calico printing, in photography, and similar minor applications. Vanadium pentoxide is also used in glass to absorb ultraviolet light, and both this compound and the metallic vanadates have been employed for coloring glass and ceramic glazes. The principal chemical use, however, is in the preparation of catalytic bodies for various oxidation reactions, chiefly in the oxidation of sulfur dioxide in the production of sulfuric acid and in the manufacture of phthalic anhydride from napthalene; these uses now consume large quantities."

Other products used in the manufacture of vanadium and uranium alloys or in other lines of industry are vanadium oxide (as high as 99% V_2O_5), sodium vanadate (as high as 66% V_2O_5), iron vanadate, uranium concentrates (as high as 67% U_3O_8), uranium oxide (99% U_3O_8), etc.

[1] Vanadium was discovered by Manuel del Rio in 1801 in the lead ores of Mexico. Thirty years later Sefstrom found the element in iron produced from the ores of Taberg in Sweden. Berzelius contributed much to the knowledge of the element.

DETECTION

Ammonium Sulfide or Hydrogen Sulfide passed into an ammoniacal solution of vanadium precipitates brown V_2S_5, soluble in an excess of alkali sulfide and in alkalies, forming the brownish-red thio-solution, from which the sulfide may be reprecipitated by acids.

Reducing Agents.—Metallic zinc, sulfites (SO_2), oxalic acid, tartaric acid, sugar, alcohol, hydrogen sulfide, hydrochloric acid, hydrobromic and hydriodic acids (KI) reduce the acid solutions of vanadates with formation of a *blue-colored* liquid. (See Volumetric Methods.) Reduction is hastened by heating.

Hydrogen Peroxide added to a cold acid solution of vanadium produces a *brown color*, changing to blue upon application of heat. See detection of vanadium in steel.

The oxide, V_2O_5, is distinguished from Fe_2O_3 by the fact that it fuses very readily with the heat of Bunsen burner, whereas the oxide of iron, Fe_2O_3, is infusible in the heat of a blast lamp. M.p. $V_2O_5 = 658°$ C.; m.p. $Fe_2O_3 = 1548°$ C.

Comparison of Vanadium and Chromium Salts.—Vanadium, like chromium, forms a soluble salt upon fusion with sodium carbonate and potassium nitrate or with sodium peroxide. The solution of vanadates and of chromates are yellow or orange; the color of the chromate becomes more intense when strongly acidified, whereas that of the vanadate is reduced. The yellow color of the vanadate solution is destroyed by boiling with an excess of alkali, but may be restored by neutralizing the alkali with acid. The chromate color is not destroyed. (Yellow with alkalies, orange in acid solution.) Silver nitrate produces a dark-maroon precipitate with a soluble chromate and an orange-colored precipitate with a vanadate; mercurous nitrate produces a red-colored precipitate with chromates and a yellow with vanadates. *Vanadates are also distinguished from chromates by the reduction test;* [2] reducing agents such as a soluble sulfite, or sulfurous acid added to acid solutions, form *a blue-colored liquid with vanadates and a green color with chromates. Ammonium hydroxide* added in excess to the cold reduced solutions gives a brown color, or a brown to dirty green precipitate with *vanadium*, and violet or lavender color or a light green-colored precipitate with *chromium*, depending upon the concentration of the solutions. Hydrogen peroxide added to the reduced cold acid solutions changes the vanadium blue to reddish brown; the chromium green remains unchanged.

Detection of Vanadium in Steel.—One gram of the sample is dissolved in dilute nitric acid, the nitrous fumes boiled off, the solution cooled, and an excess of sodium bismuthate added. After filtering through an asbestos filter an excess of concentrated ferrous sulfate solution is added, and the solution divided into two equal parts in test-tubes. To one portion 10 ml. of hydrogen peroxide are added and to the other 10 ml. of water. If vanadium is present the peroxide solution will show a deeper color than the untreated solution. A deep red color is produced with high vanadium steels and a brownish-red with low. Since titanium also causes this color, it would interfere, if it were not for the fact that

[2] Reduction with zinc is rapid with vanadates, much less vigorous with chromates. V_2O_5 reduced to V_2O_2, color changes to blue, green, lavender and finally violet. SO_2 or H_2S reduces V_2O_5 to V_2O_4. V_2O_2 forms vanadyl salts.

the color produced with titanium is destroyed by hydrofluoric acid and fluorides, whereas that of vanadium is not. In presence of titanium, 5 ml. of hydrofluoric acid are added to the treated sample.

The brown color produced by hydrogen peroxide, with vanadium solutions, will remain in the water portion when shaken with ether. The ether layer is colored a transient blue in presence of chromium.

"Hydrogen peroxide is the most satisfactory test for general work. Iron, an element usually associated with vanadium, offers little interference. Titanium and large amounts of molybdenum will give trouble, but the first mentioned can be taken care of with hydrofluoric acid. Hydrogen sulfide gas passed through a vanadate made alkaline with ammonia gives a red color to the solution. This is the most sensitive test we know for vanadium. Unfortunately, many of the common elements precipitate or render the test useless unless previously removed. With some experience, the operator can detect .01% V providing the steel contains not more than small amounts of chromium and no titanium. The chromium reduces the sensitivity of the test due to the pronounced green color of its reduced [3] salts."

ESTIMATION

The materials in which the estimation of vanadium is desired are essentially ores, metallurgical products, and chemical products.

In the process of analysis in presence of considerable ferric iron vanadium is quantitatively precipitated by NH_4OH leading to an error in the iron and aluminum determination unless accounted for. If aluminum alone is present the precipitation of vanadium is not complete. NH_4OH alone does not precipitate vanadium. The oxide, V_2O_5, may be mistaken for Fe_2O_3, but its low melting point (V_2O_5 658° C.) enables it to be easily distinguished from that of iron.

PREPARATION AND SOLUTION OF THE SAMPLE

While many vanadium and uranium ores can be completely, or almost completely, decomposed by treatment with mineral acids, the only universally applicable method of decomposition consists in fusion with sodium peroxide. Because of the presence of carbonaceous matter and free sulfur in patronite, this ore is best decomposed by the last-mentioned method. Vanadinite, descloizite, mottramite, etc., can in general be decomposed with acids. Roscoelite is not readily souble in acids. Carnotite is easily soluble even in cold dilute mineral acids, but some of the vanadium minerals that accompany it are not (Hillebrand).

Element.—The metal is not attacked by aqueous alkalies, but is soluble by fusion with potassium or sodium hydroxide, and sodium carbonate containing

[3] L. E. Harper.

potassium nitrate. It is insoluble in dilute hydrochloric and sulfuric acids. It dissolves in concentrated sulfuric acid and in dilute and concentrated nitric acid forming blue solutions.

Oxides.—V_2O_2 is easily soluble in dilute acids, giving a lavender-colored solution.

V_2O_3 is insoluble in hydrochloric and sulfuric acids, and in alkali solutions. It dissolves in hydrofluoric acid, and in nitric acid.

V_2O_4 is easily soluble in acids, forming blue-colored solutions. It dissolves in alkali solutions.

V_2O_5 is soluble in acids, alkali hydroxide and carbonate solutions. Insoluble in alcohol and acetic acid.

Salts.—Ammonium meta vanadate, NH_4VO_3, is slightly soluble in cold water, readily soluble in hot water. The presence of ammonium chloride renders the salt less soluble. The vanadates of lead, mercury and silver are difficultly soluble in water. These are dissolved, or are transposed by mineral acids, the vanadium going into solution; i.e., lead vanadate treated with sulfuric acid precipitates lead sulfate and vanadic acid passes into solution.

General Procedure for Decomposition of Ores.—One gram (or more) of the finely divided material is placed in a large platinum crucible together with five times its weight of a mixture of sodium carbonate and potassium nitrate ($Na_2CO_3 = 10$, $KNO_3 = 1$). The product is heated to fusion over a blast lamp and, when molten, about 0.5 to 1 gram more of the nitrate added in small portions. (Caution—platinum is attacked by KNO_3. A large excess of Na_2CO_3 tends to prevent this.) The material should be kept in quiet fusion for ten to fifteen minutes, when most of the ores will be completely decomposed. The cooled fusion is extracted with boiling water, whereby the vanadium goes into solution. Arsenic, antimony, phosphorus, molybdenum, tungsten and chromium pass into solution with the vanadium. These must be removed in the gravimetric determination of this element. (Iron remains insoluble in the water extract.)

Should there be any undecomposed ore, the residue from the water extract will be gritty. If this is the case, a second fusion with the above fusion mixture should be made.

Small amounts of occluded vanadium may be recovered from the water-insoluble residue by dissolving this in nitric acid and pouring the solution into a boiling solution of sodium hydroxide. Vanadium remains in solution.

Vanadium may be determined volumetrically after removal of the hydrogen sulfide group, by titration with potassium permanganate according to the procedure given later. The isolation and determination of vanadium by the gravimetric procedures are given in detail later.

Ores and Material High in Silica.—The sample is treated in a platinum dish with about ten times its weight of hydrofluoric acid (10 to 50 ml.) and 2 to 5 ml. of concentrated sulfuric acid. The silica is expelled as SiF_4 and the hydrofluoric acid driven off by taking the solution to SO_3 fumes. The residue is extracted with hot water containing a little sulfuric acid. Any undissolved residue may be brought into solution by fusion with potassium acid sulfate, $KHSO_4$, and extraction with hot water containing a little sulfuric acid. By this treatment the iron passes into solution with vanadium.

Products Low in Silica.—Decomposition may be effected by fusion in a nickel crucible with sodium peroxide and extraction with water. The water should be added cautiously, as the reaction is vigorous. One gram of the finely divided ore is intimately mixed with 3 to 4 grams of Na_2O_2 and 1 gram of the peroxide placed on the charge. The material is then fused as stated.[4]

Iron and Steel.—The solution of the sample, isolation of vanadium and its volumetric determination are given at the close of the chapter.

Alloys.—These may be decomposed with nitric acid, or aqua regia. The isolation of vanadium with mercurous nitrate or lead acetate are given under the gravimetric methods.

SEPARATIONS

Fusion with sodium carbonate and potassium nitrate and extraction of the melt with water effect a separation of vanadium from most of the metals, which remain insoluble as carbonates or oxides. Arsenic, molybdenum, tungsten, chromium and phosphorus, however, pass into the filtrate with vanadium.

Removal of Arsenic.—This element generally occurs in vanadium ores. It may be removed when desired, by acidifying the water extract of the fusion with sulfuric acid, and after reducing arsenic with SO_2, precipitating the sulfide, As_2S_3 with H_2S gas. Vanadium passes into the filtrate.

Removal of Molybdenum.—The procedure is similar to that used for arsenic. The solution is treated with H_2S. It is advisable to resaturate the solution with H_2S before filtering off the sulfide. Some vanadium invariably accompanies the molybdenum on the first precipitation of molybdenum when separating from large amounts of vanadium.

Separation from Phosphoric Acid.—In the gravimetric procedure phosphorus and vanadium are precipitated together as mercurous vanadate and phosphate. The mercury is expelled by heat and the oxides V_2O_5 and P_2O_5 weighed. (V_2O_5 in presence of P_2O_5 does not melt as it does in pure form, but only sinters.) The oxides are fused with an equal weight of sodium carbonate, the melt dissolved in water, then acidified with sulfuric acid and vanadium reduced to the vanadyl condition by SO_2 gas. The excess of SO_2 is expelled by boiling and passing in CO_2, then cooled to room temperature and phosphoric acid now precipitated with ammonium molybdate (50 ml. of a solution containing 75 grams ammonium molybdate dissolved in 500 ml. of water and poured into 500 ml. nitric acid—sp.gr. 1.2) in presence of a large amount of ammonium nitrate and a little free nitric acid. It is advisable to dissolve the precipitate in ammonia and reprecipitate in presence of additional ammonium molybdate

[4] Direct reduction and titration of vanadium in presence of a large accumulation of salts leads to erroneous results. The vanadium should be separated by precipitation with lead acetate.

and nitrate by acidifying with nitric acid. The equivalent P_2O_5 is deducted from the weight of the combined oxides, the difference being due to V_2O_5.

NOTE.—Vanadium must be completely reduced to the vanadyl form, as vanadic acid will precipitate with phosphoric acid.

Separation of Vanadium and Chromium.—A volumetric procedure for determining vanadium and chromium in the presence of one another is given. If a separation is desired the following procedures may be used:

A. The solution is acidified with nitric acid. If hydrochloric acid is present it is expelled by taking to near dryness twice with nitric acid, the residue is taken up with water and SO_2 gas passed in to completely reduce the vanadium. This solution is poured into a boiling solution of 10% sodium hydroxide. After boiling a few minutes, the solution is filtered and the residue washed. The filtrate contains vanadium, the residue chromium. It is advisable to pour the filtrate into additional caustic to remove the small amount of chromium that passes into the solution.

B. One hundred ml. of the neutral solution is made acid with about 15 ml. of glacial acetic acid and hydrogen peroxide added. The solution is boiled for a few minutes. Chromium is thereby reduced to Cr_2O_3, whereas vanadium appears as V_2O_5. Lead acetate will now precipitate lead vanadate, the reduced chromium remaining in solution. The lead vanadate now treated with concentrated sulfuric acid is decomposed upon heating. Addition of water precipitates $PbSO_4$, the vanadium remaining in solution.

Separation of Vanadium by Precipitation with Cupferron.—This method is more efficient, consumes less time, and is the basis of separating numerous other elements. The chromium having been reduced to the trivalent condition by hydrogen peroxide, alcohol, or sulfur dioxide, and the excess expelled, cupferron (6% water solution) is then added to a 4% H_2SO_4 solution of the two metals. Complete precipitation of V is indicated by the appearance of a milky white precipitation. This separation should be conducted in cold solutions, i.e., 0° to 20° C.

GRAVIMETRIC METHODS

The following procedures presuppose that vanadium is present in the solution as an alkali vanadate, the form in which it occurs in the water extract from a fusion with sodium carbonate and potassium nitrate, as is described in the method of solution of ores containing vanadium. Chromium, arsenic, phosphorus, molybdenum and tungsten, if present in the ore will be found in this solution.

Vanadium is best determined by volumetric methods. The following procedures may have occasional use.

MERCUROUS NITRATE METHOD FOR DETERMINATION OF VANADIUM—GRAVIMETRIC [5]

Principle.—A nearly neutral solution of mercurous nitrate precipitates vanadium completely from its solution. The dried precipitate ignited forms the oxide, V_2O_5, mercury being volatilized.

Procedure.—To the alkaline solution or an aliquot portion of the water extract from the sodium carbonate potassium nitrate fusion nearly neutralized with nitric acid [6] (the solution should remain slightly alkaline) is added drop by drop, a nearly neutral solution of mercurous nitrate in slight excess of that necessary to precipitate completely the vanadium present, as may be determined by allowing the precipitate to settle and adding a few drops more of the reagent. The mixture is heated to boiling and then placed on the water bath or steam plate and the gray-colored precipitate allowed to settle. The precipitate is washed several times with water containing a few drops of mercurous nitrate, washing once or twice by decantation and finally on the filter paper. The precipitate is dried, then ignited in a porcelain crucible in a hood over a Bunsen burner to a red heat. The fused red residue is V_2O_5.

$$V_2O_5 \times 0.5602 = V.$$

GRAVIMETRIC METHOD OF DETERMINING VANADIUM BY PRECIPITATION WITH LEAD ACETATE [7]

Principle.—From a weakly acetic acid solution, vanadium is quantitatively precipitated by lead acetate. The precipitate is dissolved in nitric acid, lead removed as a sulfate, and vanadium determined in the filtrate by taking to dryness and igniting to the oxide, V_2O_5.

Procedure.—To the alkaline solution or an aliquot portion obtained by extraction of the carbonate fusion of the ore with water, just sufficient amount of nitric acid is added to nearly neutralize the alkali present, as in the case of the method described for precipitation of vanadium by mercurous nitrate, and then a 10% solution of lead acetate is added in slight excess with continuous stirring. The precipitate is allowed to settle on the steam bath. The vanadate, first appearing orange colored, will fade to white upon standing. The lead vanadate is filtered and washed free of the excess of lead acetate with water containing acetic acid. The precipitate is washed into a porcelain dish with a little dilute nitric acid, and brought into solution by warming the lead salt with nitric acid. To this, the ash of the incinerated filter is added. Sufficient sulfuric acid is added to precipitate completely the lead, and the solution taken

[5] Method of Rose. J. W. Mellor, "A Treatise on Quantitative Inorganic Analysis."

[6] Should the alkaline solution of the vanadate be made acid, nitrous acid, from the nitrate fusion, will be liberated and cause reduction of the vanadate to the vanadyl salt, in which form it is not precipitated by mercurous nitrate; hence great care should be used in neutralizing the alkaline solution to avoid making it acid. It is a good practice to measure the acid added, having determined on an aliquot portion the amount necessary to add to neutralize the solution. This is readily accomplished when a comparatively large sample has been prepared for analysis and an aliquot portion taken for analysis, several determinations being made on the same fusion.

[7] Method by Roscoe, Ann. Chem. Pharm., Supplement 8, 102, 1872. Treadwell and Hall, "Analytical Chemistry."

to small volume on the water bath and then to SO_3 fumes, but not to dryness. About 100 ml. of water are added and the mixture filtered; lead sulfate will remain upon the filter and the vanadium will be in solution. The lead sulfate is washed free of vanadium (i.e., until the washings no longer give a brown color with hydrogen peroxide).

The filtrate containing all the vanadium is evaporated to small volume in the porcelain dish, then transferred to a weighed platinum crucible and evaporated to dryness on the water bath and finally the residue (V_2O_5) heated to a dull redness over a Bunsen flame.

$$V_2O_5 \times 0.5602 = V.$$

NOTES.—Lead may be separated from the vanadium by passing H_2S through the nitric acid solution, the excess of H_2S volatilized by boiling and the liberated sulfur filtered off. The filtrate is evaporated to dryness and the vanadium ignited with a few drops of nitric acid to the oxide V_2O_5.

Lead may also be separated as lead chloride in the presence of alcohol, the solution taken to dryness and vanadium oxidized by addition of nitric acid and ignited to V_2O_5.

VOLUMETRIC PROCEDURES FOR THE DETERMINATION OF VANADIUM

REDUCTION OF THE VANADATE, V_2O_5, TO VANADYL CONDITION, V_2O_4, AND REOXIDATION WITH POTASSIUM PERMANGANATE

Principle.—Vanadium in solution as a vanadate is reduced to the vanadyl salt by H_2S or SO_2, the excess of the reducing agent expelled and the solution titrated with standard $KMnO_4$, vanadium being oxidized to its highest form, V_2O_5.

Reactions.—*a.* $V_2O_5+SO_2=V_2O_4+SO_3$. *b.* $V_2O_4+O=V_2O_5$. Hence

$$N/10 \text{ sol.} = \frac{\text{At.wt. V}}{10} \text{ grams per liter.}$$

Procedure.—An aliquot portion of the solution containing vanadium, as obtained by one of the procedures given for the solution of the sample, is taken for analysis; dilute sulfuric acid (1 : 1) is added to acid reaction and 5 ml. of acid per 100 ml. of solution added in excess. The vanadium content should be not over 0.5 gram V when a tenth normal permanganate is used for the titration. *If arsenic or molybdenum is present* these may be removed from the solution by passing in H_2S, although molybdenum does not interfere. The insoluble sulfides are filtered off and washed with H_2S water. The filtrate is boiled down to two-thirds of its volume and the sulfur filtered off. In the absence of members of the H_2S group, this portion of the procedure is omitted. Before reduction of vanadium, should H_2S have been used, it is necessary to first oxidize polythionic compounds by addition of $KMnO_4$ to a faint pink color. See below.

Oxidation with $KMnO_4$.—The solution containing the vanadium is oxidized by adding, from a burette, tenth normal potassium permanganate to a faint permanent pink. If the solution has been treated with H_2S, the vanadium is in the vanadyl condition, and the amount of permanganate required to oxidize the solution completely will give a close approximate value for the vanadium present, each ml. of N/10 $KMnO_4$ being equivalent to 0.0051 gram vanadium.

Reduction.—The vanadate is now reduced to vanadyl salt by passing through the acid solution, containing approximately 5% free sulfuric acid, a steady stream of SO_2 gas. Reduction may also be accomplished by adding sodium metabisulfite, or sodium sulfite, to the acid solution. The excess SO_2 is now removed by boiling (a current of CO_2 passed into the hot solution will assist in the complete expulsion of the SO_2).

NOTE.—$KMnO_4$ is reduced by SO_2.

Test for Iron.—A drop test with potassium ferricyanide, $K_3Fe(CN)_6$, on a white tile will give a blue color in the presence of ferrous iron. Since ferrous iron will titrate with potassium permanganate, its oxidation is necessary. This is accomplished by adding tenth normal potassium dichromate solution cautiously to the cold liquid until no blue color is produced by the spot test with $K_3Fe(CN)_6$ outside indicator. If the sample is sufficiently dilute, the blue color of the vanadyl solution will not interfere in getting the point where the iron is completely oxidized. Care must be taken not to pass this end-point, otherwise V_2O_4 will also be oxidized and the results will be low.

NOTE.—The action of the dichromate is selective to the extent that iron is first oxidized and then V_2O_4. If the amount of iron present is large a separation must be effected. In case a sodium carbonate potassium nitrate fusion has been made and vanadium has been extracted by water, iron will not be present. A special procedure for determination of vanadium in steel is given.

Potassium Permanganate Titration.—N/10 $KMnO_4$ is now cautiously added until a pink color, persisting for one minute, is obtained. During the titration the solution changes from a blue color to a green, then a yellow and finally a faint pink. The reaction towards the end is apt to be slow if made in a cold solution.

NOTES.—In absence of chromium, it is better to make the titration in a hot solution, 60 to 80° C., the end-point being improved by heat. In case an excess of permanganate has been added, the excess may be determined by a back titration with tenth normal thiosulfate. The solution may be rerun, if desired, by repeating the reduction with SO_2 and the titration with $K_2Cr_2O_7$ and $KMnO_4$.

One milliliter N/10 $KMnO_4$ = 0.005095 gram V, or = 0.009095 gram V_2O_5.

For solutions containing less than 0.5% vanadium a weaker permanganate reagent should be used. A fiftieth normal permanganate solution will be found to be useful for materials low in vanadium.

The author obtained excellent results by the above procedure on materials containing small amounts of iron and chromium; with amounts equal to that of vanadium present in the solution no interference was experienced. The titration with potassium permanganate is made in cold solutions if chromium is present, as the permanganate will oxidize chromium in hot solutions. Potassium permanganate added to samples containing chromic salts, and the mixture boiled, will oxidize these quantitatively to chromates. This reaction does not take place in cold solutions to any appreciable extent during a titration and only slowly in warm solutions.

VOLUMETRIC DETERMINATION OF VANADIUM BY REDUCTION WITH ZINC TO V_2O_2

The procedure proposed by Gooch and Edgar is to reduce vanadic acid, in presence of sulfuric acid, by zinc to the oxide, V_2O_2; oxidation of the unstable V_2O_2 by the air is anticipated by means of ferric chloride or sulfate, in the receiver of the Jones reductor, the highest degree of reduction being registered by the ferrous salt formed by the reaction of the reduced vanadate on the ferric salt, i.e., $V_2O_2+3Fe_2O_3=6FeO+V_2O_5$. Compounds reduced by zinc and oxidized by $KMnO_4$ must be absent or allowed for.

Procedure.—The Jones reductor is set up as directed in the procedure for the determination of iron by zinc reduction. The receiver attached to the tube containing the column of zinc is charged with a solution of ferric alum in considerable excess of that required for the oxidation of the reduced vanadium. (The amalgamated zinc is cleaned by passing through the column, a dilute solution of warm sulfuric acid. The final acid washings should show no further reducing action on permanganate when the reductor is clean.)[8] Gentle suction is applied, and through the column of clean amalgamated zinc are passed in succession—100 ml. of hot water, 100 ml. of 2.5% sulfuric acid, and then the solution of vanadic acid diluted to 25 ml. in a 2.5% sulfuric acid solution, and finally 100 ml. of hot water. To the receiver is added a volume of 4 ml. of syrupy phosphoric acid to decolorize the solution. The reduced iron salt is now titrated with N/10 $KMnO_4$.

One ml. N/10 $KMnO_4$ = 0.001698 gram V, or = 0.003032 gram V_2O_5.

VOLUMETRIC DETERMINATION OF MOLYBDENUM AND VANADIUM IN PRESENCE OF ONE ANOTHER

Sulfur dioxide reduces V_2O_5 to V_2O_4, but does not reduce molybdic acid provided the sample contains 1 ml. of free sulfuric acid per 50 ml. of solution and not more than 0.2 gram of molybdic acid. By means of amalgamated zinc V_2O_5 is reduced to V_2O_2 and MoO_3 to Mo_2O_3. Upon these two reactions the determination is based according to the procedure worked out by Edgar.[9] Details of the method are given in the chapter on Molybdenum.

VOLUMETRIC DETERMINATION OF VANADIUM, ARSENIC OR ANTIMONY IN PRESENCE OF ONE ANOTHER. EDGAR'S METHOD[10]

Tartaric or oxalic acid reduces V_2O_5 to V_2O_4, but does not act upon arsenic or antimony. On the other hand SO_2 causes the reduction of all three. There-

[8] Corrections should be made for the action of zinc upon the reagents without the vanadic acids, as it is almost impossible to get a condition where no blank is obtained with permanganate. The reductor is cleaned first by passing about 500 ml. of dilute 2.5% sulfuric acid through the column of zinc. A blank is now obtained with the same quantity of reagents as is used in the regular determination, only omitting the vanadium, and this is deducted from the titration obtained for each sample reduced.

[9] Graham, Edgar, Am. Jour. Sci. (4), **25**, 332. Gooch, "Methods in Chemical Analysis," John Wiley & Sons.

[10] G. Edgar, Am. Jour. Sci. (4), **27**, 299.

fore if aliquot portions of the solution are taken, one portion being treated with tartaric acid and vanadium determined by titration with iodine, and another portion reduced with SO_2 and again titrated with iodine, the difference between the two titrations is due to the ml. of reagent required for the oxidation of the reduced arsenic or antimony.[11]

Reactions.—

$$V_2O_4+I_2+H_2O=V_2O_5+2HI.$$
$$As_2O_3+V_2O_4+3I_2+3H_2O=As_2O_5+V_2O_5+6HI.$$
$$Sb_2O_3+V_2O_4+3I_2+3H_2O=Sb_2O_5+V_2O_5+6HI.$$

Vanadium.—One portion is boiled with about 2 grams of tartaric or oxalic acid, until the solution turns the characteristic blue of vanadium tetroxide. After cooling, the solution is nearly neutralized with potassium bicarbonate, and an excess of standard iodine solution added. Neutralization is now completed, an excess of bicarbonate added, and after fifteen to thirty minutes the excess iodine titrated with standard arsenious acid, starch being used as an indicator. This titration measures the vanadium present.

Arsenic or Antimony.—A second portion of the solution is placed in a pressure flask and acidified with sulfuric acid. A strong solution of sulfurous acid is added, the flask closed and heated for an hour on the steam bath. After cooling, the flask is opened and the solution transferred to an Erlenmeyer flask and the excess of SO_2 removed by boiling, a current of CO_2 being passed through the liquid. The cooled solution is treated with bicarbonate, iodine added and the titration conducted exactly as described for determination of vanadium in the first portion. The difference between the first titration and the second is a measure of the ml. required for oxidation of arsenic or antimony.

DETERMINATION OF VANADIUM AND IRON IN PRESENCE OF EACH OTHER

The solution slightly acidified with sulfuric acid is treated with sulfurous acid, the excess expelled and the reduced vanadium and iron titrated with standard potassium permanganate.[12]

$$10FeO+5V_2O_4+6H_2SO_4+4KMnO_4$$
$$=5Fe_2O_3+5V_2O_5+2K_2SO_4+4MnSO_4+6H_2O.$$

The solution is now reduced with zinc in the Jones reductor and again titrated with permanganate.[11] V_2O_5 is reduced by zinc to V_2O_2, the sample being caught in ferric alum solution (details for determining of vanadium by reduction with zinc are given under the volumetric methods for this element).

$$10FeO+5V_2O_2+12H_2SO_4+8KMnO_4$$
$$=5Fe_2O_3+5V_2O_5+4K_2SO_4+8MnSO_4+12H_2O.$$

The difference between the two titrations multiplied by 0.00455 = vanadic acid (V_2O_5) originally present.

[11] Gooch, "Methods of Chemical Analysis."
See Am. J. Sci. (4), 27, 174, also Gooch, "Methods in Chemical Analysis," p. 510, for procedure determining iron, chromium and vanadium, in presence of one another.

[12] When the color has changed from a bluish-green to greenish-yellow the solution is heated to 70 to 80° C., and the permanganate titration completed in a hot solution.

IODOMETRIC METHOD FOR ESTIMATION OF CHROMIC AND VANADIC ACIDS IN PRESENCE OF ONE ANOTHER

The following procedure developed by Edgar,[13] is given by Gooch ("Methods of Chemical Analysis").

In carrying out the operation, the alkali salts of the chromic and vanadic acid are put into the Voit flask of the distillation apparatus shown in the cut, Fig. 127.

One or 2 grams of potassium bromide are added, the flask is connected with the absorption apparatus containing a solution of potassium iodide made alkaline with sodium carbonate or sodium hydroxide, and the whole apparatus is filled with hydrogen gas. Fifteen to 20 ml. of concentrated hydrochloric acid are added through the separatory funnel and the solution is boiled for ten minutes, an interval of time found to be enough for the completion of the

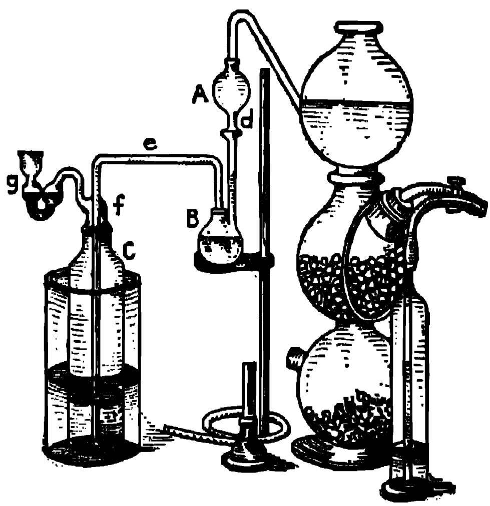


FIG. 127. Voit Flask and Distilling Apparatus.

reduction. A slow current of hydrogen is maintained to avoid back suction of the liquid from the Drexel bottle. The apparatus is disconnected, the Voit flask placed in a beaker containing cold water, and the alkaline solution in the absorption apparatus cooled by running water. The contents of the trap are washed into the Drexel bottle and the solution therein is made slightly acid with hydrochloric acid. The liberated iodine is titrated with approximately N/10 sodium thiosulfate and the color is brought back by a drop or two of N/10 iodine solution, after the addition of starch.

Alkaline potassium iodide is again placed in the absorption apparatus and the latter connected with the Voit flask. The current of hydrogen is turned on and, after the air has been expelled, the apparatus is disconnected momentarily, 1 or 2 grams of potassium iodide are added to the solution in the Voit flask, and connections made again. Through the separatory funnel 10 ml. to 15 ml. of concentrated hydrochloric acid and 3 ml. of syrupy phosphoric acid are

[13] Graham Edgar, Am. J. Sci. (4), 26, 333.

added and the solution in the reduction flask is boiled to a volume of 10 ml. to 12 ml. The absorption apparatus is removed and cooled, hydrochloric acid is added and the liberated iodine titrated with approximately N/10 sodium thiosulfate.

The iodine determined in the first titration corresponds to a reduction of the chromic and vanadic acids according to the equation

$$V_2O_5+2CrO_3+8HBr=V_2O_4+Cr_2O_3+4Br_2+4H_2O,$$

while in the second case the iodine corresponds to a reduction of the vanadium tetroxide to trioxide as indicated in the equation

$$V_2O_4+2HI=V_2O_3+I_2+H_2O.$$

The second titration, therefore, determines the vanadic acid present, and the difference between the first and second furnishes the necessary data for the calculation of the chromium.

ANALYSIS OF VANADIUM ORES

The high prices of vanadium and uranium ores and products make it important when the analytical results are to be used as the basis for buying or selling, that the most accurate known methods should be used. It is fortunate, therefore, that some of the most dependable methods are also capable of yielding quite rapid results. Needless to say, work of this character, where large sums of money are involved, should be entrusted only to an experienced and skillful analytical chemist.

THE DETERMINATION OF VANADIUM AND URANIUM IN CARNOTITE AND VANADIFEROUS URANIUM ORES

From one to 5 grams of the 100-mesh sample, the amount used being determined by the uranium and vanadium contents of the ore, are treated with from 20 to 60 ml. of hydrochloric acid (sp.gr. 1.19) in a 600-ml. beaker provided with a clock-glass cover. The solution is heated at a temperature of about 60° C. until the reaction appears to be complete. Approximately 2 grams of potassium chlorate are added and the solution is boiled for a few minutes. Twelve ml. of sulfuric acid (sp.gr. 1.84) are then introduced and the liquid is evaporated until fumes of sulfur trioxide are given off. When the beaker and its contents have cooled, approximately 50 ml. of water are added and the solution is boiled until all soluble salts have dissolved, when it is filtered on an 11-cm. paper into a 250-ml. beaker. The residue of silica, lead sulfate (if the ore contains lead), etc., is washed thoroughly with 1% sulfuric acid and treated as described in the next paragraph.

Inasmuch as carnotite is easily soluble in acids there is little likelihood of uranium being held back in the siliceous residue. However, some of the western carnotite ores contain vanadium in combinations which are not so readily broken up by acids, consequently unless experiments on the type of ore being analyzed have shown that the acid treatment extracts all uranium and vanadium it is necessary to treat the insoluble residue as further described. If the ore contains lead the lead sulfate is dissolved out of the siliceous residue with ammonium acetate. This is accomplished by returning the paper and precipitate to the original beaker, adding an excess of a 25% solution of ammonium acetate and a few ml. of ammonia, and heating the liquid to boiling. After having beaten the paper to a pulp with a glass rod, the contents of the beaker are transferred to an 11-cm. paper and the filter and residue are washed thoroughly with a hot, slightly ammoniacal 10% solution of ammonium acetate. The filter and its contents are ignited in a porcelain crucible at a low red heat until the carbon of the filter paper has been oxidized, when the residue is transferred to a large platinum crucible. Approximately 2 ml. of nitric acid (sp.gr. 1.42) and 5–10 ml. of hydrofluoric acid (48%) are added and the solution is evaporated slowly to dryness. If much quartz is present the treatment with nitric and hydrofluoric acids is repeated. One ml. of sulfuric acid (1 to 1) is then added and the crucible is heated until sulfur trioxide is freely expelled. The residue is dissolved in water and added to the main solution. Fusion of the residue with potassium pyrosulfate should be used only as a last resort, as the presence of potassium sulfate is objectionable in the subsequent operations.

The procedure described in the preceding paragraphs insures the solution of all uranium and vanadium and the removal of silica and lead. The solution, which should have a volume of approximately 200 ml. (an acidity of 5%), is heated nearly to boiling and saturated with hydrogen sulfide, which will result in the vanadium being reduced to the quadrivalent form and copper and other metals of the copper group being precipitated as sulfides. If arsenic is present the hot liquid should be given a prolonged treatment with the hydrogen sulfide. Some ashless paper pulp is added and the solution is filtered on an 11-cm. paper into a 400-ml. beaker. The precipitate of copper sulfide, etc., is washed with 1% sulfuric acid containing hydrogen sulfide and either used for the determination of copper or discarded.

The filtrate from the copper sulfide, etc., which will contain all of the uranium, vanadium, iron, aluminum, magnesium, phosphorus, etc., is boiled to expel most of the hydrogen sulfide and to reduce the volume to about 100 ml. The di-vanadyl sulfate, ferrous sulfate, free sulfur, any remaining hydrogen sulfide, etc., are then oxidized by adding to the hot liquid a *slight excess* of a strong solution (25 grams per liter) of potassium permanganate. The volume of the solution is then determined by comparison with a measured amount of water in another 400-ml. beaker; the essential thing is that the acidity of the solution be adjusted so that approximately 10 ml. of sulfuric acid (sp.gr. 1.84) are present in each 100 ml. of solution, which end can be accomplished by either evaporation or dilution. If the acidity is not properly regulated uranium will be held back with the vanadium or the vanadium will not be completely precipitated. The beaker and its contents are then cooled to approximately ten degrees Centigrade.

To the solution obtained as described in the preceding paragraph there is added a slight excess of a cold, freshly prepared, 6% solution of cupferron (ammonium nitrosophenylhydroxylamine, $C_6H_5N(NO)ONH_4$). This will cause the complete precipitation of the vanadium and iron, while uranium, zinc, aluminum, calcium, magnesium, phosphorus, etc., will remain quantitatively in solution. As soon as a drop of the reagent causes the formation of a transsient snow-white crystalline precipitate, the reaction is complete. Some ashless paper pulp is added and the precipitate is filtered on an 11-cm. paper and washed fifteen or eighteen times with cold 10% H_2SO_4. It is necessary that a record be kept of the volume of H_2SO_4 introduced into the filtrate in the wash solutions. Both the precipitate and the filtrate are reserved.

The vanadium precipitate is treated for the determination of the vanadium by one of the following procedures:

(*a*) The precipitate is ignited carefully in a platinum crucible and fused with four or five grams of potassium pyrosulfate. The fusion is dissolved in the least necessary amount of water and the solution is transferred to a 300-ml. Erlenmeyer flask. An excess of strong $KMnO_4$ solution (25 grams per liter.) and 15 ml. of sulfuric acid (sp.gr. 1.84) are added and the solution is evaporated until fumes of sulfur trioxide are given off. The vanadium is then reduced by evaporation with hydrochloric acid and determined by titration with 0.05 N potassium permanganate as described on p. 1046.

(*b*) The precipitate is ignited in an iron crucible, fused with four or five grams of sodium peroxide and determined by the Ammonium Persulfate Method as described on p. 1048.

The filtrate and washings from the vanadium and iron precipitate are boiled down to a volume of about 50 ml., 30 ml. of nitric acid (sp.gr. 1.42) are added, and the evaporation is continued until fumes of sulfur trioxide are freely given off. Several small additions of ammonium persulfate, made after the solution has been evaporated to a low volume but before sulfur trioxide has begun to come off, will aid materially in the destruction of the organic compounds present. The solution is then evaporated until strong fumes of sulfur trioxide are evolved. When the beaker and its contents have cooled 120 ml. of water are added and the solution is heated until all salts have dissolved. The next step in the process consists in the reduction of the uranium to the quadrivalent (UO_2) condition preliminary to its precipitation with cupferron as described in the next paragraph.

If the weight of uranium in the sample exceeds 0.3 gram, 2 grams of zinc (containing 0.002% or less iron) are added and the solution is warmed until most of the zinc has dissolved, which will result in the partial reduction of the uranium. When working with ordinary carnotite ores this step is unnecessary. The solution is cooled to *room temperature* (20 to 25° C.) and passed through a Jones reductor having a zinc column about 10″ long. All uranium is washed out of the zinc column by passing 130 ml. of water through the reductor. Approximately six minutes are as a rule consumed in passing the uranium solution and the wash water through the reductor.

The reduced solution, which should have a volume of 250 ml. and consequently an acidity of approximately 6%, is transferred to a 400-ml. beaker cooled to 5° to 10° C., and treated with an excess of a cold, freshly prepared, 6% solution of cupferron. If the solution contains less than 4 ml. of sulfuric

acid (sp.gr. 1.84) per 100 ml. the uranium precipitate will drag down aluminum and phosphorus, while if the amount of acid exceeds 8 ml. per 100 ml. of solution, the precipitation of the uranium will not be quantitative. For this reason it is important that the amount of acid present in the solution be known and that the acidity be adjusted to approximately 5% by appropriate dilution. The precipitate does not begin to form until from five to ten ml. of the reagent have been added. If uranium is present it will be completely thrown down as a brown crystalline precipitate having the composition $U(C_6H_5N_2O_2)_4$. Some ashless paper pulp is added and the precipitate is filtered on a 9-cm. paper and washed eighteen or twenty times with cold 4% sulfuric acid. Aluminum, chromium, manganese, calcium, magnesium, phosphorus, and zinc (from the reductor) pass quantitatively into the filtrate.

The precipitate is ignited in a large weighed platinum crucible at a *very low red heat* until the carbon has been destroyed. The presence of the paper pulp is quite essential since it causes the precipitate to form a porous, friable mass, easily penetrated by air or oxygen, thus rendering it much easier to burn off the carbon and oxidize the uranium to U_3O_8. The temperature is then increased to 1050° to 1100° C. for approximately 15 minutes. The crucible and its contents are cooled in a desiccator and weighed. Multiplication of the weight of the uranoso-uranic oxide, U_3O_8, by 0.8481 and divided by the weight of sample taken, gives the percentage of uranium in the sample.

If desired, the result obtained by weighing the U_3O_8 can be checked by fusing the precipitate with a small amount of potassium pyrosulfate and dissolving the fusion in 100 ml. of 6% sulfuric acid. If the amount of uranium exceeds 0.3 gram, the solution is given a preliminary reduction by adding 2 grams of zinc (0.002% or less iron). The solution is cooled to room temperature passed through a Jones reductor, stirred vigorously for from three to five minutes, and titrated with 0.05 N or 0.1 N potassium permanganate (each ml. equals 0.005955 or 0.01191 gram uranium) which has been standardized against sodium oxalate obtained from the Bureau of Standards. The time required for passing the solution and 100 ml. of wash water through the reductor is approximately five minutes.

In titrating a uranium solution with permanganate it is necessary to determine a "blank" on the reductor and reagents and, in addition, a "blank" is run to determine the volume of permanganate required to produce a pink color to the yellow solution of the uranyl sulfate. The "blank" (usually about 0.1 ml.) on the reductor and reagents is conducted in exactly the same way the determination was made except that 100 ml. of 6% sulfuric acid is substituted for the uranium solution. The "blank" (varies with the amount of uranium involved; however, not more than 0.1 ml. of 0.1 N $KMnO_4$ is required to produce a pink tint to a solution containing 0.3000 gram uranium) is run in the following manner: In a regular analysis after reducing and titrating the uranium, the solution is treated with several drops (sufficient amount to discharge the pink color of the permanganate) of approximately 0.1 N solution of ferrous ammonium sulfate, and the excess of ferrous iron over that required to destroy the excess of permanganate is oxidized by adding 8 ml. of 15% ammonium persulfate solution and *stirring the solution vigorously for one minute.* The reaction that occurs is shown by the following equation:

$$2FeSO_4+(NH_4)_2S_2O_8=Fe_2(SO_4)_3+(NH_4)_2SO_4.$$

A 0.1 N solution of potassium permanganate is then carefully run into the liquid with constant stirring until the first permanent pink tinge appears. The volume of 0.1 N $KMnO_4$ required to produce the pink color constitutes the "blank" due to the yellow color of the uranyl sulfate.

Therefore, in a regular analysis, the volume of 0.1 N $KMnO_4$ remaining after deducting the "blank" on the *reductor, reagents* and *that due to the influence of yellow color of the uranyl sulfate, multiplied by .01190,* gives the weight of uranium in the sample.

THE HYDROCHLORIC ACID REDUCTION METHOD FOR THE DETERMINATION OF VANADIUM

This method is recommended as being excellent for the determination of vanadium (no provision is made for the determination of uranium) in vanadinite, mottramite, or other ores or concentrates which can be completely or almost completely decomposed with acids. The process was originally proposed by Campagne and modified and perfected by A. M. Smoot of Ledoux & Company, who discovered that the reduction of the vanadium to the quadrivalent form is complete even in the presence of a large amount of sulfuric acid *provided sufficient ferric iron is present.* None of the elements ordinarily found in vanadium ores, including copper, zinc, or arsenic, even when present in large amounts, interfere.

From two to 5 grams of the 100-mesh sample of the ore or concentrate, the amount used being determined by the vanadium content, are heated in a 600-ml. covered beaker with from 40 to 60 ml. of hydrochloric acid (sp.gr. 1.19) at a temperature of 50 to 60° C. until the decomposition appears to be complete. To oxidize any carbonaceous matter, potassium chlorate is next added, a little at a time, until a total weight of about 2 grams has been introduced. Twenty ml. of sulfuric acid (1 to 1) are added and the solution is evaporated until fumes of sulfur trioxide are freely evolved. Approximately 100 ml. of water are then introduced cautiously and the solution is boiled and filtered into a 500-ml. Erlenmeyer flask. The precipitate of lead sulfate, silica, etc., is treated to recover any vanadium as given in the second paragraph of Method 1, the solution of any material remaining after the lead sulfate has been extracted and the silica volatilized being added to the Erlenmeyer flask containing the main solution.

Five ml. of nitric acid (sp.gr. 1.42) are added to the sulfuric acid solution containing all of the vanadium and the liquid is evaporated to a volume of approximately 40 ml. A sufficient volume of a solution of potassium permanganate (25 grams per liter) to give a strong pink color is next introduced from a dropping bottle, and the evaporation is continued until fumes of sulfur trioxide appear. After having allowed the flask and its contents to cool somewhat, 20 ml. of sulfuric acid (1 to 1) and 50 ml. of hydrochloric acid (sp. gr. 1.19) are added in the order mentioned. A weight of ferric sulfate or chloride containing *a weight of iron approximately equal to that of the vanadium present in the solution of the ore* is next introduced and the solution is then boiled down to a volume of about 30 ml. Twenty-five milliliters of hydrochloric acid (sp.gr. 1.19) are added and the liquid is boiled down as rapidly as possible without causing "bumping" until the hydrochloric acid has been

expelled and sulfur trioxide begins to come off. The flask is kept on the hot plate for a period of 10 minutes at a sufficiently high temperature to cause the rapid expulsion of sulfur trioxide, when it is removed and allowed to cool. Long continued fuming (more than twenty minutes) will cause the re-oxidation of some of the quadrivalent vanadium to the quinquivalent state. Approximately 50 ml. of cold water and five ml. of phosphoric acid (syrup, sp.gr. 1.72) are then added and the solution is diluted with hot water to 350 ml., heated until all soluble matter has dissolved, cooled, and titrated at 20°–25° C. with 0.05 N or 0.1 N potassium permanganate (the former for low vanadium and the latter for high vanadium products) which has been standardized against pure sodium oxalate obtained from the Bureau of Standards. The completion of the reaction is marked by the development of a pink color *which remains permanent for 30 seconds.*

The "blank" (usually about 0.1 ml.) is run in the following manner: In a regular analysis after completing the determination, the solution is immediately treated with one drop (*just sufficient amount* to discharge the pink color of the permanganate) of approximately 0.1 N ferrous ammonium sulfate, and the excess of ferrous iron over that required to destroy the excess of permanganate is oxidized by adding 8 ml. of 15% ammonium persulfate solution and *stirring the solution vigorously for one minute.* The reaction that occurs is shown by the following equation:

$$2FeSO_4+(NH_4)_2S_2O_8=Fe_2(SO_4)_3+(NH_4)_2SO_4.$$

A 0.1 N solution of potassium permanganate is then carefully run into the liquid with constant stirring until the first permanent pink tinge appears. The volume of 0.1 N $KMnO_4$ required to produce the pink color constitutes the "blank" due to the yellow color of the vanadic acid.

FUSION METHOD FOR THE DETERMINATION OF VANADIUM IN ORES CONTAINING ONLY SMALL AMOUNTS OF COPPER OR ZINC[14]

This method, which can be used for the determination of vanadium in any of its ores except those containing significant amounts of copper or zinc, includes no provision for the determination of uranium. It is especially applicable to roscoelite, vanadiferous sandstones, or ores which contain large amounts of carbonaceous matter.

From one gram of the 100-mesh sample, the amount used being regulated by the vanadium content of the ore, are fused with 15 grams of sodium peroxide in a 40 ml. pure iron crucible. The crucibles are stamped from No. 20 gauge (0.32″) thickness pure iron purchased in the form of sheets 12″ wide by 12′ long from the American Rolling Mill Co., Middletown, Ohio. The contents of the crucible are fused carefully over the flame of a laboratory burner or in an electric furnace. The fusion is best accomplished by holding the crucible with a pair of tongs and slowly revolving it around the outer edge of the flame until the contents have melted down quietly, care being taken not to raise the temperature so rapidly as to cause spattering. When the fusion is molten, a

[14] Method of the Electro Metallurgical Company.

slight rotary motion is imparted to the crucible to stir up any unattacked particles of ore on the bottom and sides, the crucible and contents being maintained at a very low red heat. Five minutes' heating is usually sufficient. Where a large (three or four gram) sample is used and difficulty is experienced in obtaining a fluid fusion, complete decomposition can often be secured by heating at a temperature just short of that necessary to melt the mixture.

When cool, the crucible is placed in a 600-ml. beaker and treated with 150–200 ml. of warm water. The reaction between the water and the excess of sodium peroxide is quite violent, consequently care should be taken to avoid loss by spattering. The crucible is removed with a pair of tongs and rinsed with a jet of hot water.

High grade vanadium oxide (about 80% V_2O_5) can often be conveniently decomposed in the following manner: Six-tenths gram of the 100-mesh sample is transferred to a 600-ml. beaker and treated with 15 ml. of water. Sodium peroxide is then added, a pinch at a time, with stirring, until decomposition appears to have been effected. The solution is then warmed slightly to complete the reaction, which required only a few minutes all told.

The advantages of the sodium peroxide fusion are that it insures complete decomposition of the ore and thorough oxidation of carbonaceous matter, free sulfur, sulfides, etc., in a single, rapid clean-cut operation.

The solution obtained as described in the preceding paragraphs is acidified with 50 ml. of sulfuric acid (1 : 1) and 15 ml. of nitric acid (sp.gr. 1.42). If the ore contains much lead, a precipitate of lead sulfate will be noticeable. Some scales of relatively inert magnetic iron oxide from the crucible will remain undissolved. The solution is then cooled to room temperature preliminary to the titration of the vanadium. The vanadium is determined by the Ammonium Persulfate Method.

AMMONIUM PERSULFATE METHOD

One to 4 grams of the ore are fused with from 8 to 15 grams of sodium peroxide and the fusion is dissolved in water, acidified with 70 ml. of sulfuric acid (1 : 1) and transferred to an 800-ml. beaker jar and diluted to 400 ml. as previously described. Ores containing high percentages of lead should be treated as described under "Method 2. The Hydrochloric Acid Reduction Method," paragraph 2.

To the acid solution of the ore obtained as described by either of the above methods there is added, with constant stirring, an approximately 0.1 N solution of $KMnO_4$ (the titer of the solution need not be known) until a strong pink color has developed which remains permanent for 30 seconds. The solution is cooled to 15° C., then an approximately 0.1 N solution of ferrous ammonium sulfate (it is unnecessary to determine the exact strength of this solution) is run in with constant stirring until a drop of the solution when added on a spot plate to a drop of a 0.1% solution of potassium ferricyanide results in the *immediate* formation of a blue color, showing that an excess of ferrous iron is present. A sufficient number of spot tests must be made so that only a comparatively small excess of the reducing agent is added. Five milliliters excess of the ferrous ammonium sulfate are then introduced and after having stirred the solution for one minute, the excess of ferrous salt over that required to reduce the vanadium is oxidized by adding 8 ml. of 15% ammonium persulfate solution and *vigorously stirring the liquid for one minute longer.* The tempera-

ture of the solution should not exceed 18° C. when the persulfate is added and the titration with standard $KMnO_4$ should be made at a temperature of 18 to 20° C. The reactions which occur are shown by the following equations:

$$2H_3VO_4+2FeSO_4+3H_2SO_4=V_2O_2(SO_4)_2+Fe_2(SO_4)+6H_2O,$$
$$2FeSO_4+(NH_4)_2S_2O_8=Fe_2(SO_4)_3+(NH_4)_2SO_4.$$

A 0.05 N or 0.1 N solution of potassium permanganate is then run into the solution with constant stirring until a faint pink color, *which remains permanent for 30 seconds*, has developed.

$$5V_2O_2(SO_4)_2+2KMnO_4+22H_2O=10H_3VO_4+K_2SO_4+2MnSO_4+7H_2SO_4.$$

The "blank" (usually about 0.1 ml.) is run in the following manner: In the regular analysis after completing the determination, the solution is immediately treated with one drop (*just sufficient amount* to discharge the pink color of the permanganate) of approximately 0.1 N ferrous ammonium sulfate, and the excess of ferrous iron over that required to destroy the excess of permanganate is oxidized by adding 8 ml. of 15% ammonium persulfate solution and *stirring the solution vigorously for one minute.* The reaction that occurs is shown by the following equation:

$$2FeSO_4+(NH_4)_2S_2O_8=Fe_2(SO_4)_3+(NH_4)_2SO_4.$$

A 0.1 N solution of potassium permanganate is then carefully run into the liquid with constant stirring until the first permanent pink tinge appears. The volume of 0.1 $KMnO_4$ required to produce the pink color constitutes the "blank" due to the yellow color of the vanadic acid.

Therefore, the volume of 0.1 N $KMnO_4$ required in the analysis, less the "blank," multiplied by 0.005096, gives the weight of vanadium in the sample.

PREPARATION AND STANDARDIZATION OF SOLUTIONS

Ferrous Ammonium Sulfate, Approximately 0.1 N.—Prepared by dissolving 49 grams of C.P. $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ in water, adding 10 ml. of sulfuric acid (sp.gr. 1.84) and making up with water to one liter at room temperature. (The exact titer of this solution need not be known.)

Potassium Permanganate, Approximately 0.1 N.—Prepared by dissolving 3.18 grams of pure $KMnO_4$ in boiling distilled water, cooling to room temperature, filtering on asbestos, making up to one liter and mixing thoroughly. The solution is standardized against pure sodium oxalate obtained from the National Bureau of Standards according to their procedure.

ANALYSIS OF FERRO VANADIUM

DETERMINATION OF VANADIUM

Treat 0.5095 of the alloy, dried to 105° C., in a 250-ml. covered beaker with 60 ml. of sulfuric acid (1 : 2) and 25 ml. of nitric acid (1 : 1). If the alloy does not decompose readily, add 2 or 3 ml. of hydrofluoric acid. When the reaction has abated, evaporate to copious fumes. Cool, add 100 ml. of water and boil until salts are in solution. Transfer the contents to a 600-ml. beaker and dilute to 300 ml. with water. Cool the solution to 15 or 20° C. Add 0.1 N potassium permanganate until very strong pink color remains for a minute, and excess does no harm. Next reduce the vanadium by the use of approximately 0.1 N ferrous ammonium sulfate added until a drop withdrawn from the beaker and placed on a drop of potassium ferricyanide shows ferrous iron present; normally this reduction will take from 35 ml. to 40 ml. of solution. Add 3 ml. to 5 ml. in excess and stir for 1 minute, oxidize the excess ferrous ammonium sulfate with 15 ml. of 10% ammonium persulfate freshly made and stir vigorously for one minute. The temperature of the solution should not exceed 18° C. when the persulfate is added and the titration with standard $KMnO_4$ should be made at a temperature of 18 to 20° C.

Titrate the solution with an 0.1 N potassium permanganate solution, added with constant stirring until a faint pink appears which will remain for 1 minute. A blank test is made by dissolving 0.59 gram of ingot iron using the same concentration of acid as the test and putting the blank through all the operations of the analysis. This blank found is subtracted from the number ml. used in the test. Having used a factor weight (0.5095 gram) the number of ml. used reads % vanadium in the alloy.

Example.—41.35 ml. 0.1 N potassium permanganate used in titration

.15 ml.	1 N potassium permanganate used in blank run
41.20 ml.	or 41.20% vanadium in the alloy.

Solutions required. ***Ammonium persulfate.***—Ten grams of the salt dissolved in 100 ml. of water.

Potassium ferricyanide.—Ten grams of salt dissolved in 100 ml. of water.

Ferrous ammonium sulfate approximately 0.1 N. Forty-nine grams of salt dissolved in water 30 ml. (1 : 3) *sulfuric acid* added and dilute to a liter.

Potassium permanganate 0.1 N. Dissolve 3.2 g. of $KMnO_4$ in 1000 ml. distilled water, allow to age for at least 10 days and filter through purified asbestos. Standardize the permanganate solution against Bureau of Standards Standard sodium oxalate. One ml. of 0.1 N $KMnO_4$ is equivalent to 0.005096 gram of vanadium in the following method.

CARBON IN FERRO-VANADIUM

1.3635 gms. of 100 mesh alloy are mixed with 2 gms. of red lead. This charge is placed on an alumdum cushion in the combustion boat. The boat is then placed in the electric furnace and burned at 1100° C. for 10 minutes. The CO_2 is absorbed in Ascarite using Midvale type bulb. A good grade of lead oxide usually contains 2 or 3 points of carbon. This blank must be determined and a correction made for carbon found in the red lead.

DETERMINATION OF SILICON

Dissolve 0.9344 (2 factor weights) using 20 ml. hydrochloric acid, 10 ml. nitric acid and 30 ml. (1–2) in a 600-ml. beaker; evaporate to copious fumes. Some samples of ferro vanadium containing silicon are not soluble in acid and must be fused. 0.4672 g. (1 factor weight) of the alloy are mixed with 6 to 8 grams of sodium peroxide in an iron crucible and thoroughly mixed. The crucible is heated over a Meker burner near the top of the mixture while rotating the crucible.

As the fusion progresses the crucible can be lowered in the hotter zone of the flame. With the proper rotation of crucible a melt can be obtained in which all the alloy is fused in about 3 minutes. The melt is allowed to cool and leached out in a platinum dish with water. The solution is acidified with hydrochloric acid and 30 ml. sulfuric acid (conc.) added and evaporated to fumes. Cool the sulfuric acid solution obtained by either procedure and add 200 ml. to 300 ml. of water and boil until all the salts are in solution. Filter on a 9-cm. paper, wash with hot hydrochloric acid (10 : 100) and hot water until iron and vanadium salts are removed and then wash free from acid with water. Transfer precipitate to a platinum crucible, ignite at 1100 to 1150° C. for 40 minutes. Weigh and purify precipitate by adding 4 drops sulfuric acid (conc.) and 10 ml. of hydrofluoric acid. Evaporate to dryness, ignite and weigh. Difference in weights divided by 2 or 1 (depending on amount taken) multiplied by 100 gives the silicon in the alloy.

DETERMINATION OF VANADIUM IN CUPRO-VANADIUM, BRASSES AND BRONZES

Dissolve 1.020 grams of cupro-vanadium in aqua regia. Evaporate to small bulk and add excess of peroxide of hydrogen. Dilute to 600 ml. and add ammonia until all copper goes into solution. Heat to boiling and add sufficient barium chloride solution to precipitate all the vanadium. Boil and filter. Wash all copper out of filter with hot ammonia water. Transfer the filter to a beaker, add 100 ml. 1 : 2 sulfuric acid, boil and filter on close filter paper. Titrate the filtrate with N/10 ferrous ammonium sulfate and N/10 potassium bichromate the same as in the case of the ferro alloy, except that this being a two-factor weight, the result must be divided by 2.

Vanadium copper, brasses and bronzes are treated in the same manner except that a ten-factor weight is used and the titration carried out with N/50 solution instead of N/10.

DETERMINATION OF VANADIUM IN STEEL

Volumetric–Phosphomolybdate Method for Determination of Vanadium

Reagents. ***Ammonium Molybdate.***—See page 700 for phosphorus in steel.

Ammonium Phosphate.—Fifty grams salt per liter of water.

Acid Ammonium Sulfate.—Fifty milliliters concentrated H_2SO_4, 950 ml. water and 15 ml. strong ammonium hydroxide. Use hot, 80° C.

Nitric Acid.—One hundred milliliters concentrated HNO_3 and 1200 ml. water.

Nitric Acid for Washing.—Twenty milliliters concentrated HNO_3 per liter.

Potassium Permanganate Standard.—0.35 g. salt per liter of solution. Standardized against sodium oxalate. Adjust so that 1 ml. will equal 0.0005 g. vanadium, or 0.02% on a 2.5-g. sample. One gram $Na_2C_2O_4 = 0.7612$ g. V.

Potassium Permanganate, for oxidation. Twenty-five grams salt per liter of solution.

Sodium Bisulfite, for reduction. Thirty grams salt per liter of solution.

Procedure for Steel.—A sample of 2.5 g. of steel in a 300-ml. beaker or Erlenmeyer flask are dissolved in 50 ml. of the nitric acid, and to the boiling solution are added 6 ml. of the permanganate oxidation solution, the boiling being continued until MnO_2 precipitates. The precipitate is now dissolved by cautious additions of sodium bisulfite solution and the boiling continued until no brown fumes are evident. Now 5 ml. of ammonium phosphate solution are added and 10 g. ammonium nitrate. The solution is removed from the heat and 50 ml. of ammonium molybdate reagent immediately added. After standing for 1 minute, the solution is agitated for 3 minutes, then allowed to settle and the clear solution decanted through an asbestos filter, the residue is washed three times with hot acid ammonium sulfate reagent, decanting each time through the filter. The flask containing the bulk of the residue is placed under the filter. (The washings are best conducted with suction, using a bell jar filter.) The precipitate on the filter is dissolved by successive portions of hot concentrated H_2SO_4, catching the solution in the vessel containing the bulk of the precipitate. The precipitate is now dissolved by heating and to the solution a few drops of the nitric acid are added and the heating continued to strong fumes.

The solution is cooled and hydrogen peroxide added in small quantities with vigorous shaking after each addition, until the solution takes on a deep brown color. The solution is again heated for 4 or 5 minutes, then cooled and 100 ml. of water added, the solution again heated to about 80° C. and titrated to a permanent pink color with standard potassium permanganate.

NOTE.—If the peroxide treatment followed by heating does not result in a clear green or blue color, the solution should be evaporated to strong sulfuric acid fumes and the peroxide treatment repeated. The presence of nitric acid interferes with the reduction of vanadium.

VANADIUM IN STEEL—ETHER EXTRACTION—HYDROCHLORIC ACID REDUCTION METHOD

Reagents. *Hydrochloric Acid.*—600 ml. concentrated HCl and 400 ml. water.

Sulfuric Acid.—Equal volumes of concentrated H_2SO_4 and water.

Other Reagents—See Phosphomolybdate Precipitation Method for Vanadium.

Procedure.—A sample of 2.5 g. of steel in a 250-ml. beaker is dissolved in 50 ml. of the HCl, and then small portions of HNO_3 added to oxidize the iron. After expelling the brown fumes by heating, the solution is cooled and transferred to an 8-oz. separatory funnel, together with the rinsings (small portions of HCl) of the beaker. Now 50 ml. of ether are added and the mixture shaken for 5 minutes. After settling for 1 minute the clear lower layer is drawn into another separatory funnel. The first funnel is treated with 10 ml. of concen-

trated HCl, again shaken vigorously and the settling repeated, the lower layer being added to the solution in the second separatory funnel. The combined solutions in the second separatory funnel are treated with 50 ml. of ether and shaken for 5 minutes, allowed to settle 1 minute and the clear lower layer drawn into a 150-ml. beaker. This aqueous solution is warmed gently to expel the ether, 25 ml. of the H_2SO_4 (1 : 1) added and the mixture concentrated to strong fumes. After cooling, 25 ml. of water are added followed by a slight excess of potassium permanganate solution and the sample heated to boiling. Fifteen ml. of concentrated HCl are added and heat applied until the solution again fumes. The heating is continued for 10 minutes. After cooling, 100 ml. of water are added, the solution heated to 80° C. and titrated with standard potassium permanganate reagent to a permanent pink color.

NOTES.—In heating the solution to expel the brown fumes of oxides of nitrogen, the solution should not be boiled.

In presence of chromium, the pink color will fade on standing owing to the oxidation of chromium. The oxidation of chromium is reduced by titrating the solution cold, but only ten seconds are allowed for the pink color to remain. A blank must be run with the same amount of chromium and allowance made for its oxidation. The blank is conveniently made by putting a suitable amount of chrome steel or chrome-nickel steel through the recommended procedure. By varying the amounts of steel and hence the amount of chromium in solution, data for a charted curve may be obtained that will be convenient for a blank deduction.

The assistance in the revision of this chapter given by Messrs. Jerome Strauss, Chief Research Engineer, and L. E. Harper, Chief Chemist, Vanadium Corporation of America, is acknowledged. Also that of Thomas R. Cunningham, Chief Chemist, for his courtesy in submitting methods standardized by the Electro Metallurgical Company for analysis of vanadium ores, which appear in this chapter.

ZINC [1]

Zn, at.wt. 65.38; *sp.gr.* 6.48 to 7.14, *m.p.* 419° C.; *b.p.* 905° C.; *oxide*, ZnO

Introductory Notes.—Although the alloys used by the Romans undoubtedly contained zinc and the name zinc was used by Paracelsus in the sixteenth century, a clear knowledge of zinc as a distinct metal was not gained until the latter part of the seventeenth century, and an additional hundred years elapsed before the metal began to assume industrial importance. Zinc is now one of the most useful of the metals. It is an important constituent of a number of alloys as brass (Zn, Cu) and German silver (Zn, Cu, Ni) and die casting alloys (Zn, Cu, Al). Granulated zinc is a necessary substance in the chemical laboratory. Its resistance to rusting makes zinc valuable as a protective coating on iron surfaces (galvanized iron). Considerable quantities of zinc are used as anodes in electrical batteries. The oxide, ZnO, is used as a pigment and chemical in rubber goods, including automobile tires, and extensively as a paint pigment. It is used in glazes, in enamels, as an ointment, as dusting powder, etc. The chloride is used as a preservative of wood. The sulfide is a valuable white pigment; with barium sulfate it forms lithopone. Recently zinc and boron have been shown to be necessary to the growth of plants.

Zinc is found in nature only in combined form. Its ores in order of commercial importance are the sulfide, zinc blend or sphalerite; the carbonate, zinc spar or smithsonite; the silicate, willemite. The following minerals are of less importance—calamine, a hydrated silicate, franklinite, a complex oxide containing iron, manganese and zinc. Certain chemical glasswares contain from 3–11% of zinc. Zinc determinations should not be made in these wares.

DETECTION

General Procedure.—Zinc is brought into solution by extraction of the ore with HCl and HNO_3. The solution is evaporated to strong fumes with an excess of H_2SO_4 and the H_2S group is separated from an acid solution containing 5 ml. of 1 : 1 H_2SO_4 in 100 ml. of solution. ZnS is precipitated by H_2S from a faintly acid solution, so that neutralization of the solution from the previous group is necessary and acidification to 0.01 N. ZnS is white.

Potassium ferrocyanide precipitates a white zinc ferrocyanide of complex composition. (See method given under Volumetric Methods.)

[1] Rewritten for the 5th Edition by L. A. Wilson, Chief of Testing Department, New Jersey Zinc Co. The original chapter was by F. G. Breyer, L. S. Holstein and L. A. Wilson.

In Presence of Iron.[2]—Transfer 10 ml. of a solution of the sample to a small beaker; add 2 ml. of 85% H_3PO_4 (sp.gr. 1.7) to eliminate interference of Fe. Add 1 drop of copper-acid solution (0.5 g. $CuSO_4 \cdot 5H_2O$, 0.5 g. concentrated H_2SO_4, 100 ml. H_2O) and stir. Add mercuric-thiocyanate mixture (8 g. $HgCl_2$, 9 g. NH_4CNS, 100 ml. H_2O), stir and allow to stand for 1 minute. Zn is indicated by a violet-colored precipitate.

Blowpipe Test.—Heat the finely powdered mineral on charcoal in the reducing flame of the blowpipe; zinc if present in amount exceeding 5% will leave an incrustation which is yellow when hot and white when cold.

Cobalt Nitrate Test.—In the ZnS test free S may make the test doubtful. To identify dissolve the H_2S precipitate in 5 ml. of 2N HNO_3. Prepare a ball of ignited asbestos, half the size of a pea, held by means of a platinum wire and dip into a solution of 0.05N $Co(NO_3)_2$ and ignite. Then dip the asbestos in the HNO_3 solution and again ignite. In presence of Zn the asbestos fiber is colored green (blue from Al).

ESTIMATION

The determination of zinc is called for in the buying and selling of ores for smelters, refuse material, e.g., from galvanizing plants, foundries, brass mills, and blast furnaces, in manufacture of brass, white metals, and alloys in general, paints and pigments, zinc chloride for preservation purposes, and in the control work of smelting of zinc and lead ores.

Preliminary.—The method to be followed in the estimation of zinc will depend largely on the nature of the material in which it occurs, the quantity present, and the experience of the analyst. Each of the methods outlined will give correct results only on the materials for which they are indicated, there being but one method recommended which is applicable to all zinciferous materials. It cannot be emphasized too strongly that each step has a definite purpose (which may not be at once apparent to the analyst making only an occasional zinc determination), and no part of the procedure should be varied or omitted, excepting after abundant experience.

Zinc compounds are readily extracted from ores by attack with acids, HCl and HNO_3, the acid insoluble residue seldom containing zinc.

During the analysis, if proper provision is not made for zinc, a portion will be occluded in the aluminum precipitate, while a portion will appear with the magnesium ammonium precipitate. Unless the ammonium hydroxide precipitate is small, zinc should be separated as sulfide from acid solution, according to the procedure described later, the hydrogen sulfide group first being removed. It should be kept in mind that copper and cadmium precipitated from 0.4 N acid solutions are apt to occlude zinc. Zinc is precipitated quantitatively from 0.01 N solution of acid.

[2] Method of W. H. Hammond, Chemist-Analyst, 17, 14 (1928).

PREPARATION OF SAMPLE

The representative sample should be ground to pass a 100-mesh screen or finer. If the material contains shot metal, it should be screened out and the percentage present calculated. It is then treated as given under heading Material Containing Metallics, page 1067.

MOISTURE DETERMINATION IN THE PULP

One of the commonest causes of differences in zinc ore analysis is the failure to take moisture determinations on the pulp sample.

In order that analyses made on the same pulp at different times and in different laboratories may be compared it is absolutely necessary that all determinations be corrected to a dry basis. It is not sufficient that the sample be dried before or after having been pulped, but a sample for moisture must be weighed out at the same time as the sample for analysis, and the analytical result corrected for the per cent of moisture found at the time of weighing. This is especially true on roasted zinc ores which contain sulfates of zinc, iron, and lime and which take up moisture quite rapidly under ordinary atmospheric conditions.

The usual temperature for drying should be 110° C., but on special ores, e.g., those containing sulfates, it is necessary to dry at 250° C., unless it is first shown that there is no loss of water above 110° C.

The determination is best made by weighing approximately two grams in a small glass-stoppered weighing tube and drying to constant weight, the weighing tube being closed with the glass stopper as soon as the tube is taken from the drying oven.

Ores.—Decomposition is best effected by attack with HCl, HNO_3 followed by the customary evaporation and separation of SiO_2. Details are given under the methods of analysis. Addition of $KClO_3$ is recommended.

Alloys.—Decomposition is effected by treatment of HCl, HNO_3 or H_2SO_4. Details are given under the methods for determining zinc in alloys.

SEPARATIONS

Silica.—Evaporate with hydrochloric acid or take to fumes of sulfuric acid. The dehydration with sulfuric acid is complete and gives silica that is easily filtered and washed.

Cadmium, Lead, Arsenic, Antimony, Bismuth and Copper.—Aluminum may be used to separate all the metals, except cadmium, the latter being only partially separated. The procedure is as given in the standard method.

The separation may also be made as follows: Evaporate the solution of the zinciferous material to fumes with 7 ml. of 1 : 2 sulfuric acid. Cool, take

up in about 50 ml. of water and warm, add 10 ml. of 10% sodium thiosulfate, boil until evolution of sulfur dioxide ceases, then filter. Cadmium if present is not completely precipitated and should be removed as CdS by precipitation with H_2S. The procedure is given under Titration in Acid Solution separating Zinc as Sulfide. If the cadmium is removed with H_2S it is not necessary to also use sodium thiosulfate since lead, arsenic, antimony, bismuth and copper are also removed.

Iron, Aluminum and Manganese.—This separation may be effected by precipitation with ammonia and bromine, providing the quantities present are small. When large amounts are present the basic acetate procedure is followed, or the zinc separated as sulfide in dilute sulfuric acid solution.

Separation of Zinc from Aluminum, Iron, Cobalt, Nickel, Manganese and Chromium by Precipitation as Sulfide.—Zinc may be precipitated as sulfide by H_2S from a solution with a hydrogen ion concentration ranging between pH 2 to pH 3. This may be accomplished in a dilute sulfuric acid solution (0.01 N) according to the procedure recommended by G. Weiss and F. G. Breyer as outlined in the volumetric method given on page 1060, or from a formic acid solution as recommended by H. A. Fales and G. M. Ware.[3] Ammonium formate and citrate are used as buffers to hold the hydrogen ion concentration during the reaction with H_2S.

$$ZnSO_4 + H_2S = ZnS + H_2SO_4.$$

The precipitate that forms in presence of dilute sulfuric acid is more readily filterable than that obtained in formic acid, according to the experience of W. W. Scott. Washing by decantation is advisable in any case.

If the removal of the hydrogen sulfide group has been made with H_2S as described under *Separations*, the H_2S is first expelled and the acid cautiously neutralized with NH_4OH until a slight precipitate forms. The acidity with H_2SO_4 is now carefully adjusted by addition of 0.1 N acid. The normality should be less than 0.01 N since the action of H_2S will increase the acidity, so that allowance should be made for this.

GRAVIMETRIC METHODS

In the analysis of ores, separation of zinc from other elements, that interfere in its determination, has been considered in previous paragraphs. Zinc is best isolated as zinc sulfide, first removing the hydrogen sulfide group in an acid concentration exceeding 0.4 N. A double precipitation is recommended, especially if copper and cadmium are present. The filtrate, boiled free of H_2S is neutralized, preferably with NH_4OH (methyl red indicator)

[3] J. Am. Chem. Soc., 41, 487 (1919).

and then acidified, dropwise, with very dilute H_2SO_4, so that the normality is less than 0.01 N in respect to this acid (0.2 ml. concentrated H_2SO_4 per liter). Zinc is now separated as ZnS by precipitation with H_2S, the solution being at room temperature. The precipitate is washed free of contamination by cold water. This treatment also applies to alloys.

This precipitate may now be converted to the oxide by ignition to a temperature of 800°–900° C. It may be converted to sulfate by dissolving in HCl and evaporating with H_2SO_4. It may be weighed as ZnS after a special treatment. It may be converted to zinc ammonium phosphate and so weighed, or ignited to pyrophosphate. It may be determined electrolytically. Further details follow.

WEIGHING AS ZINC OXIDE

Zinc is separated from interfering elements as outlined above. The zinc sulfide is filtered into a weighed Gooch crucible and washed. It is now ignited, preferably in a muffle furnace at a temperature of 900° C. for an hour and weighed as ZnO. Since the oxide is hygroscopic, cooling must be effected in a desiccator and the weighing done rapidly.

$$ZnO \times 0.8034 = Zn$$

WEIGHING AS SULFATE

The zinc sulfide obtained as outlined above, after washing free of impurities, is dissolved in hydrochloric acid and the chloride treated in a weighed crucible with a slight excess of sulfuric acid. The solution is very cautiously evaporated to fumes of H_2SO_4, then cooled and a few drops of water added and the evaporation repeated, heating finally to 500° C.

$$ZnSO_4 \times 0.4050 = Zn.$$

NOTE.—At 650° C. the sulfate starts to decompose to ZnO and SO_3. It may be completely converted to the oxide by heating to 900–950° C.

WEIGHING AS THE PHOSPHATE

The phosphate method is generally considered to be the most accurate of the gravimetric methods. The determination is applicable for determining zinc in ores and in alloys. In the analysis of a copper alloy such as brass the filtrate from the copper determination is taken for the estimation of zinc. Zinc is precipitated as phosphate from a neutral solution containing ammonium salts. From a cold solution a product of doubtful composition, probably the normal phosphate $Zn_3(PO_4)_2$, an amorphous compound precipitates on addition of the phosphate reagent. On heating to 60°–90° C. the precipitate becomes crystalline and a compound having the formula $Zn(NH_4)PO_4 \cdot H_2O$ is formed. The precipitation of zinc phosphate occurs *only in a neutral solution*. since the compounds are soluble in small concentrations of either hydrogen ions or ammonium hydroxide. The crystalline product loses its water of crystallization at 105° C. On strong ignition the pyrophosphate, $Zn_2P_2O_7$ is formed.

Procedure.—The solution containing the zinc, free from elements of the previous groups and from elements precipitating as phosphates (see notes), is carefully neutralized by adding NH_4OH or HCl drop by drop using litmus paper or methyl orange as indicator. The volume of the solution should be 50–100 ml. per 0.1 g of Zn present. Heat the solution nearly to boiling and add slowly a large excess of filtered diammonium hydrogen phosphate, $(NH_4)_2HPO_4$, reagent (15 ml. of 10% solution per 0.1 g. Zn present). Heat gently until the precipitate becomes crystalline (more reagent may be necessary since about 12 times the theoretical amount is advisable). Allow the solution to cool.

Filter off the precipitate in a weighed Gooch crucible (filter paper will do. See notes). Wash with a 1% $(NH_4)_2HPO_4$ solution and finally with 50 ml. of cold water or 50% solution of alcohol.

Dry the precipitate at 105° C. for an hour and weigh as $Zn(NH_4)PO_4$. Multiply by $0.3664 = Zn$. If preferred ignite at low heat at first and then at a cherry red and weigh as $Zn_2P_2O_7$.

$$Zn_2P_2O_7 \times 0.4290 = Zn.$$

NOTES.—Preparation of diammonium hydrogen phosphate reagent. Dissolve 15 grams of the salt in a little water. This is sufficient for over 1 gram of zinc. Carefully neutralize with NH_4OH, added drop by drop, using phenolphthalein indicator. Dilute to 140 ml.

If filter paper is used in place of the Gooch crucible it is necessary to ignite the filter paper separately from the precipitate.

If precipitation is conducted in a cold solution the amorphous $Zn_3(PO_4)_2$ is formed. In presence of ammonium salts on heating the crystalline $Zn(NH_4)PO_4 \cdot H_2O$ forms.

The solubility of the compound is about 5 mg. per liter of water (20° C.). The solubility is very much less in 50% alcohol.

Free ammonia must not be present as the soluble complex cation $Zn(NH_3)_4^{++}$ would form.

In the analysis of brass the tin, lead and copper have been removed as SnO_2, $PbSO_4$ and Cu. If iron is present it is precipitated as $Fe(OH)_3$ and filtered off. Zinc is determined in the filtrate. In the analysis of an ore on removal of previous group elements Zn is isolated as ZnS from a formic or a 0.01 N sulfuric acid solution to separate it from elements of the following groups. The sulfide is dissolved in HCl and zinc now determined in a neutral solution. If there has been an exceptionally large accumulation of ammonium salts in operations prior to the zinc determination these should be destroyed by the standard method of evaporation with nitric and hydrochloric acids before precipitating the zinc ammonium phosphate.

ELECTROLYTIC METHODS

The determination is best made from an alkaline solution or one slightly acid with acetic acid and containing a considerable amount of sodium acetate. The alkaline solution tends to give high results, due to the presence of zinc oxide or hydroxide in the deposit. The best results are obtained with a solution weakly acid with one of the weaker organic acids. The procedure for the use of acetate is as follows:

The zinc is separated from other elements by precipitating with hydrogen sulfide in dilute sulfuric acid solution, as given under the standard method. The precipitate is filtered and washed, dissolved in hot hydrochloric acid—5 ml. 1 : 1 sulfuric acid added and the whole evaporated to fumes to expel hydrochloric acid. Cool and dilute, neutralize with sodium hydrate solution, make slightly alkaline, then acidify with acetic acid, and add about 5 grams of sodium acetate. The volume of solution should now be about 100 to 125 ml. Electrolyze with a platinum gauze electrode with 0.5 ampere per 100 sq. cm.

The electrolytic methods, on account of the special apparatus needed, the experience and care necessary to get reliable results, and the unavoidable errors involved in their use, are less desirable than the gravimetric oxide method and still less desirable than the ferrocyanide method.

VOLUMETRIC METHODS

STANDARD METHOD

Titration in Acid Solution—Separating Zinc as Sulfide

General.—The method of separating zinc as sulfide in a solution slightly acid with sulfuric acid is of almost universal application and can be used on any class of zinciferous material that has come under the author's observation. The steps fit together, so that copper and cadmium are easily separated and any zinc in the insoluble state, e.g., spinels, etc., can readily be looked for. The method of decomposing (taking to fumes of sulfuric acid) tends to take into solution material that would be overlooked in the rapid decompositions effected in other methods. Moreover, the use of the internal indicator gives a very sharp end-point, so that this method is fully as accurate as any gravimetric method. The method is more time consuming than other methods given, but it is not designed for rapid routine work, but rather as a standard procedure that will give absolutely reliable results on all classes of material. This method is also recommended for routine work in case the analyst is called on to make only occasional zinc analyses.

Solutions Required.—***Sulfuric Acid 1 : 1.***—Mix equal volumes of H_2SO_4 (sp.gr. 1.84) and water.

Sodium Hydroxide.—Dissolve 20 g. of C.P. NaOH in 100 ml. of water.

Sulfuric Acid 1 : 4.—Mix 200 ml. of 1 : 1 H_2SO_4 with 300 ml. of water.

Sulfuric Acid 5%.—Mix 10 g. of H_2SO_4 (sp.gr. 1.84) with 200 ml. of water.

Hydrochloric Acid 1 : 4.—Mix 250 ml. of HCl (sp.gr. 1.20) with 1000 ml. water.

Potassium Ferrocyanide.—Dissolve 34.8 g. of $K_4Fe(CN)_6$ (C.P.) in 1000 ml. of water.[4] Add 0.3 g. of $K_3Fe(CN)_6$ before using.

[4] The factor of the ferrocyanide solution will decrease with aging; more rapidly at first because of oxidation by dissolved air. Hence it is advisable to allow the solution to age for a week or two before using. For accurate work it is necessary to standardize the solution daily.

Ferrous Sulfate.—Dissolve 1.25 g. of $FeSO_4 \cdot 7H_2O$ in water, add 3 ml. of HCl (sp.gr. 1.20) and dilute to 250 ml. Add about 1 g. of powdered aluminum.

Method.—Weigh 1.0–1.5 g.[5] of sample into a tall 150-ml. pyrex (or similar zinc-free glass) beaker, add 15 ml. of HCl (sp.gr. 1.20) and 5 ml. of HNO_3 (sp.gr. 1.42) and boil moderately in a covered beaker for one half hour. Wash off cover glass and sides of beaker, add 15 ml. of 1 : 1 sulfuric acid and evaporate to strong fumes of sulfuric acid. Cool, wash down sides of beaker, rub insoluble from bottom of beaker, dilute to 50 ml. and add 0.5 g. of zinc free 20 mesh aluminum.[6] Boil for 15 minutes, or until water white, cool and transfer to a 200-ml. graduated flask. Wash out beaker thoroughly, and make up to mark in flask. Mix well and filter through a dry filter paper. Pipette 100 ml.,[7] into a tall 400-ml. beaker. Add NaOH solution until just alkaline, add 1 : 4 sulfuric acid until neutral to methyl orange and then 3 ml. of 5% H_2SO_4. Dilute to 200 ml. and pass a steady stream of hydrogen sulfide gas through for 40 minutes and let settle for 10 minutes. Filter through a 11-cm. filter paper and wash precipitate and paper twice with cold water. Then place original 400-ml. beaker under funnel, punch hole in filter paper and wash precipitate back into beaker with hot water. Put the H_2S gas tube into a small beaker with 10 ml. of HCl (sp.gr. 1.20) and hot water, to dissolve the coating of ZnS. Wash down filter paper with this HCl solution, then wash filter paper and funnel stem three times with hot 1 : 4 HCl and hot water. Boil off hydrogen sulfide, add 13 ml. of NH_4OH (sp.gr. 0.90), neutralize with HCl (sp.gr. 1.20) and add 3 ml. excess. Dilute to 200 ml., heat to boiling and titrate as under standardization.

Standardization of Potassium Ferrocyanide Solution

Method.—Weigh into tall 400-ml. beakers several portions of C.P. zinc[8] ranging from .30 to .35 g. Cover with water and dissolve on warm plate with 10ml. of HCl (sp.gr. 1.20). Cool, add 13 ml. of NH_4OH (sp.gr. 0.90), neutralize[9] with HCl (sp.gr. 1.20) and add 3 ml. in excess. Dilute to 200 ml. and heat to boiling. Add 0.3 ml. of ferrous sulfate solution. Pour about one-quarter of the solution into a 200-ml. beaker and run the standard potassium ferrocyanide solution, while stirring, into the remaining portion to a considerable excess. Add all excepting 1 to 2 ml. of the solution in the 200-ml. beaker and continue the addition of standard solution until the end point is passed by a few drops.[10] Add the remainder of the solution in the 200-ml. beaker

[5] The amount of sample taken should be such that .25 g. to .35 g. of Zn are titrated. When the desired amount is not present it is necessary to add additional $K_3Fe(CN)_6$ to produce the proper end point colors. The addition of three drops of a 1% solution of $K_3Fe(CN)_6$ before titrating is recommended.

[6] Granulated aluminum should be tested for zinc. In case ore carries copper, it is well to add a few drops of a saturated solution of sodium thiosulfate. Cadmium is partially precipitated but goes back in solution.

[7] The 100-ml. pipette should be graduated to deliver one-half the contents of the 200-ml. flask.

[8] Zinc sticks (C.P.) are rolled down to about .010″ thickness and the surface cleaned by wiping with gasoline.

[9] Use a small piece of litmus paper.

[10] Stir vigorously at this point to complete all the reactions.

and wash out with water. Continue the titration one to two drops at a time until the end point is reached.[11]

To Separate Cadmium as Sulfide.—After measuring 100 ml. of the filtrate add 5 ml. of 1 : 1 sulfuric acid and pass a rapid stream of hydrogen sulfide through the solution for fifteen minutes. Add dilute ammonia, a drop at a time until yellow cadmium sulfide precipitates. Then heat the solution to 70° to 90° C. and continue to pass hydrogen sulfide for a few minutes. Filter at once through a close paper previously packed by washing with a polysulfide, an acid and water.[12] The precipitate is washed with cold 8 to 10% sulfuric acid and finally with hot water. The filtrate is boiled to remove hydrogen sulfide, cooled, neutralized and the zinc sulfide precipitated as in the method.

Procedure for Materials Containing High Iron and Manganese.—The ZnS precipitate prepared as above will be contaminated with iron and manganese when the sample contains excessive amounts of these elements. As iron interferes with the end point and manganese will titrate in similar manner to zinc neither may be present in the solution to be titrated. The quantity of iron and manganese contamination may be reduced to a negligible amount by slightly increasing the acid concentration of the solution before precipitation. For materials high in iron and manganese add 5 ml. excess of 5% H_2SO_4 in place of 3 ml. excess given above. A second precipitation of the ZnS precipitate will serve the same purpose.

Procedure with Material Containing Insoluble Zinc.—Proceed as usual up to point where the solution is to be reduced. Filter off the silica and insoluble material, wash with hot water and reserve the filtrate. Burn the insoluble residue in a platinum crucible, taking the usual precautions in case lead is present. Fume off the silica with hydrofluoric and sulfuric acids and fuse with sodium carbonate. Dissolve in water and sulfuric acid and add to the filtrate above and proceed as in the regular method.

Discussion on Separating Zinc as Zinc Sulfide and Titrating in Acid Solution

Precipitation.—The method of precipitating zinc as sulfide in sulfuric acid solution was investigated by G. Weiss (Inaugural Dissertation, München, 1906), and the work confirmed by F. G. Breyer. The main points of Weiss' paper are as follows:

(1) "Sulfate solutions are preferable to chlorides." A N/10 chloride solution is not completely precipitated by H_2S. Furthermore, the precipitate of sulfide from HCl solution when quantitative is not crystalline and easy to filter like that obtained from sulfate solution.

[11] The change of color from blue to pea green is very sharp. It should be observed by looking down through the solution and not from the side. The change in color may be explained as follows: the few tenths of a milligram of ferrous iron added acts with the ferricyanide giving the ferro-ferricyanide blue as long as the ferrocyanide is not in excess. When it is in excess the blue is decomposed and gives the colorless ferro-ferrocyanide.

[12] All the cadmium is separated, except about 0.05%, which does not interfere with the titration at the given acidity.

(2) " The concentration of a sulfate solution is without influence on the completeness of precipitation from N/10 down. That is for solutions containing at most 400 milligrams ZnO per 100 ml."

(3) " Sulfate solutions of 400 milligrams ZnO per 100 ml. may be N/100 acid with H_2SO_4 before beginning the precipitation." Even at acidity N/20 before precipitation less than a milligram of zinc remains unprecipitated. According to Weiss, if the solution were diluted to 300 ml., 1.3 g. of H_2SO_4 could be added or 6½ ml. of 20% H_2SO_4, and still have the precipitation complete. Even if as much as 10 ml. of 20% acid were added the loss would still be only a little more than 1 milligram. Precipitating 300 milligrams from 100 ml., however, only 100 milligrams or ½ ml. of 20% acid could be added. This means that when the solution becomes more acid than 550 milligrams of H_2SO_4 per 100 ml. the precipitation of ZnS ceases. Knowing approximately the zinc content of a solution one can easily calculate the H_2SO_4 freed when the $ZnSO_4$ is converted into ZnS, and the difference between 550 milligrams and this calculated H_2SO_4 is the amount of acid that may be added when precipitating from 100 ml. of solution. For 200 ml. of course more acid can be added, being the difference between 1.100 g. and the calculated H_2SO_4 freed from the $ZnSO_4$. One and one-half times the amount of Zn judged to be present is close enough for the H_2SO_4 freed.

(4) " The precipitation, under the above given conditions, is incomplete when a slow current of hydrogen sulfide is used (about four bubbles per second). One must work with as fast a stream as possible without causing mechanical losses (at least eight bubbles per second)." Weiss is the first one to discuss this all-important question in the precipitation of ZnS. His explanation of the efficacy of the rapid stream of H_2S is as follows:

The precipitation takes place according to the following equation:

$$ZnSO_4 + H_2S \leftrightarrows ZnS + H_2SO_4.$$

Equilibrium is reached, i.e., the velocity becomes equal in both directions, and precipitation ceases when the amount of H_2SO_4 per 100 ml. reaches a certain point, under a given set of conditions. Let these conditions remain exactly the same with the exception of the H_2S and have the active mass of that increased. The equilibrium will be displaced from left to right and as a consequence ZnS will come down in the presence of more acid than before. H_2S is not very soluble in water at room temperature, but if one increases the surface of contact between the two the H_2S is dissolved much more rapidly and consequently the mass of H_2S active at any time greatly increased. This is exactly what is accomplished when the zinc solution is constantly kept full of bubbles of H_2S. One can easily see how greatly increased the mass of H_2S would be in the extreme case, when the solution is all foam.

(5) " A strong current of gas, like that called for above, will precipitate the usual amounts of zinc used in analytical operations in forty minutes."

(6) " At temperatures above 50° the precipitation is incomplete; furthermore, at room temperature the ZnS comes down in a form suitable for filtration."

(7) " Water only is required for washing the precipitates."

RAPID METHODS

Titration in Acid Solution with Outside Indicator[13]

General.—This method is especially adapted to material low in silica, alumina, iron, and manganese. When the operator gains experience in manipulation, it is possible to obtain good results on samples higher in these elements, but its haphazard use with materials high in these impurities is one of the chief causes of the common inaccuracy of zinc work. If copper or cadmium are present in quantities, the titration in acid solution, separating Zn as ZnS, is to be preferred for accurate work.

Solutions Required.—Extraction Solution.—200 g. of commercial ammonium chloride dissolved in a mixture of 500 ml. of ammonia (sp.gr. 0.90) and 750 ml. of water.

Wash Solution.—100 g. of C.P. ammonium chloride, 50 ml. of sp.gr. 0.90 ammonia. Dissolve and dilute to 1 liter.

Standard Ferrocyanide.—$K_4Fe(CN)_6 \cdot 3H_2O$ 21.6 g. to the liter. 1 ml. =about 0.005 g. Zn or 1%. Standardize on about 0.2 g. of pure zinc. Dissolve in 10 ml. of HCl. Dilute somewhat, neutralize, complete the dilution, heat and titrate precisely as described below. No filtration or H_2S water is necessary.

Method.—Weigh 0.5 g. of ore into an 8 oz. Erlenmeyer flask. Add 5 ml. of HCl and 10 ml. of HNO_3. Boil gently almost to dryness. Remove from the heat and add 12 ml. of HNO_3 and 5 g. (measured) of $KClO_3$. Boil gently just to dryness, finishing by manipulating the flask (in holder) over a free flame.

Add 35 ml. of Extraction Solution and heat to boiling, boiling very gently until disintegration is complete. Now add 10–25 ml. of saturated bromine water, according as manganese contents appear low or high, as indicated by brown color of residue. Boil a minute or two longer and then filter through an 11-cm. filter containing a small moistened wad of absorbent cotton in the apex. Receive filtrate in a 400-ml. beaker. Wash out the flask with hot water. Remove adhering residue with rubber-tipped glass rod, or dissolve it with a few drops of HCl, then add 5 ml., or an excess, of NH_4OH and rinse into filter, finally washing out flask several times with hot water. Now wash filter and residue 10 times with hot Wash Solution.

Add a little litmus paper to filtrate as indicator, stir and cautiously add HCl just to acidity, then 3 ml. in excess. Dilute, if necessary, to 200–250 ml. with hot water and heat nearly to boiling. Now add 50 ml. of saturated H_2S water and then the hot liquid is ready for titration.

Pour off about half the liquid as a reserve and titrate the balance until the end-point is passed. Use a spot-plate in which about 2 drops of a 15% solution of uranium nitrate have previously been placed in each depression. Transfer the zinc solution to the spot-plate with a glass tube instead of a rod, taking only a drop or two for each test, except for the final tests of the titration, when about ¼ of a ml. should be taken. After the first end-point is passed add a portion of the reserve and again pass the end-point. Repeat this, each time with more caution, until the reserve is reduced to about 5 ml. Now titrate,

[13] The above method, suggested by A. H. Low, is commonly used in zinc ore assays in the middle west.

6 drops at a time, until the end is again observed, then pour the entire liquid, or most of it, over the 5 ml. of the remaining reserve and then back into the same beaker again and finish the titration 2 drops at a time until the end-point, or brown tinge, is plainly apparent. Read the burette. Allow a couple of minutes for the tests to fully develop and then deduct from the burette reading for as many tests as show and for 1 drop additional. Multiply the number of ml. of ferrocyanide solution used by the percentage value of 1 ml.

NOTES.—Potassium chlorate is added to precipitate the manganese and to dilute the mass with salts facilitating the subsequent zinc extraction. The presence of HCl is undesirable, hence an excess of HNO_3 should be present to expel HCl during evaporation. Bromine water is added to insure complete precipitation of manganese.

The degree of acidity is important as it has a direct influence on the end point. Two drops (i.e. one drop excess) are necessary to produce a color at the end point, hence the deduction of one drop is made.

The zinc compound formed has approximately the following composition: $K_2ZnFe(CN)_6 \cdot Zn_2Fe(CN)_6$, the precipitating reagent is $K_4Fe(CN)_6 \cdot 3H_2O$, two molecules of this reagent (422.37 g.×2) precipitate three atoms of zinc (65.38×3) hence a reagent containing 21.54 g. is equivalent to 5 g. of zinc or to 0.005 g. Zn per ml.

During the titration with potassium ferrocyanide with too rapid addition of the reagent a false end-point is obtained. This is recognized by the fact that an additional amount of reagent causes no deepening of the brown color with the uranium indicator. With additional reagent, heating and stirring no further brown color is produced. When the true end-point is reached an addition of more ferrocyanide results in a deeper color of the spot test. The solution stirred and boiled still gives the test.

If considerable copper and lead are present in the ore, it is advisable to remove these from the solution. The addition of paper pulp assists in the settling of the sulfides, enabling a test to be made with the clear supernatant solution. With the dark suspended sulfides a sharp end-point can not be obtained, so that it is advisable to allow the solution to settle and test using the clear liquor. H_2S present in large amount interferes.

Diphenylamine Indicator for Titration

General.—In both of the previous methods the zinc may be determined by titration with potassium ferrocyanide using diphenylamine for an internal indicator as proposed by Cone and Cady [14] and slightly modified by Kolthoff.[15]

Solutions Required.—***Diphenylamine Indicator.***—Dissolve 1 g. of diphenylamine in 100 ml. of sulfuric acid (sp.gr. 1.84).

Sulfuric Acid (30%)—mix 208 ml. of H_2SO_4 (sp.gr. 1.84) with 500 ml. of water and dilute to 1 liter.

Standard Ferrocyanide.—Dissolve 21.6 g. of $K_4Fe(CN)_6 \cdot 3H_2O$ and 0.3 g. of $K_3Fe(CN)_6$ in 1000 ml. of water and standardize with C.P. zinc.

Method.—The final solutions are neutralized with either NH_4OH (sp.gr. 0.90) or H_2SO_4 (30%) depending on the previous method used. An excess of 15 ml. of H_2SO_4 (30%), 10 g. of NH_4Cl and 2 drops of the indicator are added. The solution is heated to 60° and titrated with standard potassium ferrocyanide until the blue color changes to a yellowish green.

At the beginning of the titration the liquid appears blue and becomes increasingly darker, until at about 0.5 ml. before the true end point is reached the solution changes suddenly to yellowish green; but on standing for a few

[14] W. H. Cone and L. C. Cady, J. Am. Chem. Soc., 49, 356 (1927).

[15] I. M. Kolthoff, Chem. Weekblad, 24, 203, Kolthoff & Furman, Vol. Analysis, II. J. Wiley & Sons, Inc., N. Y., 1929.

seconds the color changes back to blue. The titration is continued drop by drop until the color changes to a yellowish green, which remains for 20 seconds.

NOTE.—In case of over titration the excess of ferrocyanide may be determined by back titration with a standard zinc solution.
The elements Cu, Co, Cd, Ni and Al should be absent from the zinc solution.

Titration in Alkaline Solution

General.—This procedure is designed for rapid routine work on roasted or oxidized ores, especially those high in silica, alumina, iron, and manganese. It should only be used on unroasted sulfides, copper, or high cadmium-bearing ores, when the operator has had long experience. It is designed to give the zinc content of materials soluble in hydrochloric or nitric acid. For materials containing insoluble zinc, the titration in acid solution, in which zinc is separated as sulfide, is preferred.

Solutions Required.—***Potassium Ferrocyanide.***—34.8 g. of pure salt in 1000 ml. of water. One ml. = approximately 0.010 g. Zn.

Ferric Nitrate.—One part of salt in 6 parts of water. It is well to add a little nitric acid to prevent hydrolysis.

Citric Acid.—One part of acid in 3 parts of water. 20 ml. of nitric acid should be added to each liter to prevent mould growth.

Method.—For ores or materials containing above 50% Zn, weigh 1.0 g. of sample into a tall 400-ml. beaker. (For lower grade materials larger sample can be taken provided the iron content in the solution to be titrated does not exceed 400 mg.) Moisten the sample with water and add 25 ml. hydrochloric acid (sp.gr. 1.20). Rotate the beaker to prevent caking. Place on a hot plate or steam bath and evaporate to dryness.[16] Add 40 ml. of nitric acid (sp.gr. 1.42), cover with a watch crystal and boil off all nitrous fumes. Then add 3 to 4 g. of $KClO_3$ and boil to a volume of about 20 ml. Cool, wash off the watch crystal and sides of the beaker and dilute to about 100 ml. Wash into a 500-ml. graduated flask, make up to the mark and shake well. Filter through a close, dry, 24 cm. qualitative paper. Return the first portions of the filtrate until the filtrate comes through clear and colorless.

Measure out 250 ml.[17] of the filtrate into a 600-ml. beaker, add ferric nitrate solution to bring the iron content up to approximately 350 mg. and proceed exactly as under standardization.

Standardization.—Weigh into 600-ml. beakers several portions of C.P. zinc ranging from 0.4 to 0.5 g. Cover with water and dissolve with 10 ml. of HNO_3 (sp.gr. 1.42). Boil gently for five minutes to remove the nitrous fumes and dilute to 250 ml. with water.

Add 10 ml. of ferric nitrate solution and 20 ml. of citric acid solution. Neutralize with NH_4OH (sp.gr. 0.90) using a piece of litmus paper as the indicator, and add 25 ml. in excess.[18] Heat just to boiling and titrate with the ferro-

[16] The temperature of the hot plate should not be over 120° C. as $ZnCl_2$ is appreciably volatile at higher temperatures.

[17] The graduated flasks should be standardized against one another so that exactly half the sample is taken.

[18] The excess NH_4OH depends on the amount of zinc present and should be varied between 25 ml. for samples containing 0.4 to 0.5 g. of zinc to a few drops excess for samples containing less than 0.05 g. of zinc.

cyanide solution, using 50% acetic acid as an external indicator placed in the depressions of a test plate.

The end-point is a change in color from yellow to green produced by the formation of ferric ferrocyanide as soon as the ferrocyanide is in excess of the zinc and the solution is acidified by the acetic acid.[19] The end point may be approached by reserving a portion of the solution in a small beaker as given under titration in an acid solution with uranium nitrate as the outside indicator.

A blank determination must be made and the value of this blank subtracted from the titrations of standardizations and samples. The blank titration is approximately 0.2 ml. Add only a few drops excess NH_4OH to the blank determination.

Procedure for Copper-Bearing Ores

Either method is recommended:

Separation of Copper by Aluminum.—The sample is treated as usual up to the point where manganese has been separated and 250 ml. of the clear filtrate measured out. Add 25 ml. of 1 : 1 sulfuric acid and evaporate to strong fumes, cool, dilute to 100 ml., add a gram or two of 20-mesh zinc-free aluminum. Heat until all the copper separates, filter, wash and proceed with the filtrate as in the regular method, after oxidizing iron with a few drops of nitric acid.

Separation of Copper by Hydrogen Sulfide.—After separation of the manganese with chlorate, sulfuric acid is added and the solution taken to fumes, as in above. Cool, dilute to 100 ml., and add sulfuric acid so that 12% is present. Warm slightly and pass hydrogen sulfide through the solution. Filter off the copper sulfide, wash, boil H_2S out of the filtrate, and proceed as in the regular method, after oxidizing iron with a few drops of nitric acid.

Material Containing Cadmium.—If the material contains cadmium in quantities sufficient to warrant separation (0.15% or more), it is best to use the titration in acid solution, separating zinc as sulfide.

Material Containing Carbonaceous Matter.—If the material under examination contains carbonaceous matter, coal, etc., it must be separated by taking to dryness with hydrochloric acid. Take up in acid and water, filter and wash, and evaporate the filtrate to dryness. Take up in nitric acid and proceed as in the regular method.

If the carbonaceous material is not removed, the manganese does not separate cleanly, due to the reducing action of carbonaceous compounds.

Procedure for Material Containing Metallics.—On account of the lack of uniformity in the case of metallic zinciferous material containing lead and iron, it is well to work on large samples. Five or 10 g. of the metallics reduced to as fine a size as possible are weighed out and dissolved in nitric acid. The nitrous fumes are boiled off and the whole made up to 500 ml. or 1000 ml. Fifty or 100 ml. are now pipetted off into a 600-ml. beaker and the zinc titrated as usual. In case the metallic portion contains manganese, which is unusual, it can be separated by the regular procedure. Copper is separated as given under Copper-bearing Ores. Material containing cadmium should be analyzed by other methods, as given under Standard Procedure.

[19] It is necessary that the acetic acid be zinc free so that it is advisable to redistill it to remove traces of zinc it may contain or have taken up by standing in glass bottles containing zinc.

DETERMINATION OF SMALL AMOUNTS OF ZINC

Turbidity Method

Solution Required.—*Standard Zinc Solution.*—Dissolve 0.1 g. of zinc (C.P.) in 10 ml. of HCl (sp.gr. 1.20) and dilute to 1000 ml. 1 ml. = 0.0001 g. Zn.

Method.[20]—Take an amount of sample such that it will contain between 0.1 and 2.0 mg. of zinc. Dissolve the sample and take to fumes of sulfuric acid as directed in the procedure of the Standard Method. Dissolve the residue in water and adjust the acidity to contain about 5% free H_2SO_4 and precipitate the heavy metals with H_2S.

Filter off the heavy metals and boil the filtrate to remove the H_2S, cool, neutralize with NH_4OH and add 10 ml. of 50% citric acid solution. Heat the solution to boiling and, if no calcium citrate separates, add small quantities of calcium carbonate at a time until a precipitate of about 1.0 g. of calcium citrate is formed. Remove from heat and pass a stream of H_2S through the solution until it has cooled. Filter the solution through a small filter paper and wash with a 2% solution of NH_4CNS. Dissolve the precipitate in 3 ml. of HCl (sp.gr. 1.20) diluted to 10 ml. with water, and wash the paper with water.

Wash the solution into a 100-ml. Nessler tube and hold until a series of the standards covering the range in which the samples fall has been prepared by measuring portions of the standard zinc solution into 100-ml. Nessler tubes. Dilute the standard and sample solutions to about 90 ml. and add 3 ml. of HCl (sp.gr. 1.20) to the standard solutions, and 2 ml. of ferrocyanide solution to all solutions. Dilute each Nessler tube to the mark and mix thoroughly. After standing for at least five minutes compare the turbidity of the standards and the sample. Calculate the percentage of zinc from the quantity of sample taken and the standard solution similar in turbidity to that of the sample.

Volumetric Method

Solutions Required.—*Potassium Ferricyanide.*—Dissolve 1 g. of $K_3Fe(CN)_6$ in 100 ml. of water.

Diphenylamine Indicator.—Dissolve 1 g. of diphenylamine in 100 ml. of H_2SO_4 (sp.gr. 1.84).

Standard Potassium Ferrocyanide.—Dissolve 7 g. of $K_4Fe(CN)_6$ in 1000 ml. of water.

Method.—Proceed as in the turbidity method. If the amount of zinc present is between 1 mg. and 50 mg. it may be titrated as follows:

Dilute the solution containing the $ZnCl_2$ to 50 ml. and heat to 60° C. Add 2 drops of potassium ferricyanide and 2 drops of diphenylamine indicator. Titrate with the standard potassium ferrocyanide. Standardize the ferrocyanide by titrating portions of a standard zinc solution in the same manner. A blank determination should be made and all titrations should be corrected accordingly.

[20] M. Bodansky, J. Ind. Eng. Chem., 13, 696 (1921).

SPECIAL METHODS

Determination of Metallic Zinc in Zinc Dust

Discussion.—There have been various methods proposed for determining the metallic zinc content of zinc dust. Most of these are based upon its reducing power. The latter may be determined by any one of many ways, although the results from different methods will not be concordant, due to the inaccuracies inherent with most of the methods. Potassium bichromate, iodate, ferric sulfate, and iodine have been used for measuring the reducing power of zinc dust. Fresenius also proposed dissolving the zinc dust in dilute sulfuric acid and after drying passing the hydrogen over heated copper oxide in a combustion tube, absorbing the water formed in a calcium chloride tube and weighing.

There have also been methods devised based on the volume of hydrogen evolved when a sample of zinc dust is resolved in dilute acid. Several investigators have concluded from comparative investigations that the gasometric determination of the hydrogen evolved gives the most consistently accurate results. The best arrangement of apparatus for carrying out this hydrogen evolution method is shown in Fig. 128. The time required for a determination is about 1½ hours.

Procedure.—One gram of zinc dust is weighed and transferred as rapidly as possible to a small Erlenmeyer flask *A*, of 100 or 200 ml. capacity, in which is placed a piece of sheet platinum about 1.5 cm. square. About 5 g. of clean unoxidized ferrous sulfate crystals are added on top of the zinc dust and the flask nearly filled with distilled water saturated at room temperature with hydrogen gas.

The object of adding the sheet platinum and ferrous sulfate is to increase the rate of hydrogen evolution by catalytic action. A further reason for adding the ferrous sulfate on top of the zinc dust sample is to coagulate the latter as much as possible when it becomes wetted, and thus prevent the floating of more than an unappreciable amount of the sample.

The rubber stopper containing separatory funnel *B* and connecting *C* is tightly inserted into the neck of the flask. A little distilled water is poured into *B* and the three-way stopcock in *C* turned to connect the flask with the downward outlet. Enough water is now run in from the separatory funnel to displace all the air in the flask and the connecting tube through the bore in its stopcock. The stopcock in *C* is now turned so that the downward outlet is in connection with the measuring tube *D*. By raising the leveling bottle *E*, containing 10% sulfuric acid also saturated with hydrogen at room temperature, all the gas in *D* is displaced. The stopcock in *C* is now turned through 90 degrees so as to connect the decomposing flask *A* with the measuring tube *D*. The system is hence completely filled with liquid and ready for the generation of hydrogen. The measuring tube *D* has a total capacity of 400 ml. and is graduated from 250 to 400 ml. by 0.25 ml.

Thirty milliliters of 1 : 1 sulfuric acid are now poured into the separatory funnel. A small portion of this acid is allowed to run into the decomposing flask until a brisk but not too rapid evolution of hydrogen takes place. The acid, being much heavier than water, settles to the bottom of the flask and

the action commences immediately. The gas evolved, together with some solution and a very small amount of zinc dust passes over into the measuring tube, displacing the acid there. When the action in the decomposing flask has slowed down, more concentrated acid is introduced until all has been added. During this time the acid in the measuring tube and flask is shaken so as to wash down the particles of zinc dust from the upper parts of the flask and tube now filled with gas. The particles in the measuring tube on coming in contact with the 10% sulfuric acid are readily dissolved and generate their portion of hydrogen.

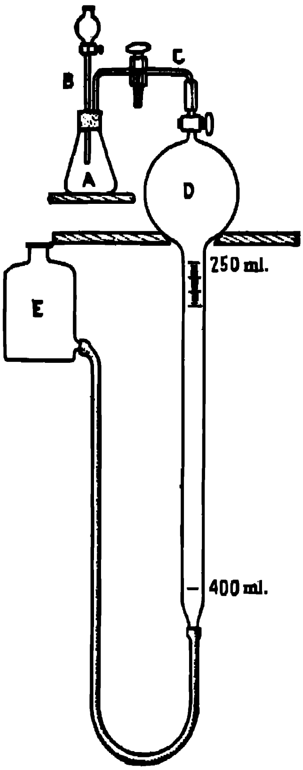


FIG. 128. Apparatus for Determining Metallic Zinc.

When all the zinc dust has been dissolved, water is run in from the separatory funnel to force the hydrogen over into the measuring tube and to fill the flask and connecting tube with water through the stopcock which is then closed. After leveling with the leveling bottle the volume of hydrogen generated from the 1-g. sample at the prevailing atmospheric conditions is read from the measuring tube. The percentage of metallic zinc in the sample is then calculated from the following expression:

Per cent of Metallic Zinc

$$= \frac{V \times (P-p-a) \times 0.29196}{(1+0.00367t)760},$$

in which V = volume of gas in measuring tube at atmospheric conditions, P = barometric pressure, p = vapor tension of water above 10% sulfuric acid at room temperature, a = temp. correction for expansion of Hg in the barometer (this is approximately $0.13t$), and t = room temperature in °C.

Necessary Precautions.—To obtain results of the highest accuracy, it is necessary when weighing out samples of zinc dust which are very finely divided, to keep the time of exposure as small as possible in order to minimize the oxidation that takes place with the oxygen of the air. It is also highly important when samples are to be held, that they be kept in ground glass stoppered bottles, completely filled, and sealed with paraffin or wax.

The two variables most likely to affect the results are temperature and barometric pressure. A change in the barometric pressure is practically always extended over a reasonable length of time. A careful reading of the barometer when the volume of gas in the measuring tube is read will eliminate any error from this source. A temperature change, on the other hand, affects not only the volume of gas, according to Charles' law, but also affects the vapor tension of water and hence the actual pressure of the hydrogen when measured.

The rubber connection between the connecting and measuring tubes must be of heavy rubber and should be shellacked.

The vapor tension of water is slightly lower above 10% sulfuric acid than above pure water, and for accurate work should be used in place of the ordinary vapor tension tables.

The result obtained should be corrected for any metallic impurities, as Fe, Al, etc., which evolve hydrogen when dissolved in sulfuric acid.

ANALYSIS OF SLAB ZINC

DETERMINATION OF IMPURITIES IN SLAB ZINC

The rejection limits of the six grades of Slab Zinc (Spelter) considered by the American Society for Testing Materials are listed in the following:

Grade	Pb Not Over	Fe Not Over	Cd Not Over	Sum Pb+Fe +Cd Not Over	Al
No. 1*a* Special High Grade....	.010%[a]	.005%	.005%	.010%	None
No. 1 High Grade...........	.07	.03[b]	.07	.10	"
No. 2 Intermediate..........	.20	.03	.50	.50	"
No. 3 Brass Special.........	.60	.03	.50	1.0	"
No. 4 Selected..............	.80	.04	.75	1.25	"
No. 5 Prime Western........	1.60	.08			

[a] Tentative limit Grade No. 1*a* Pb .007% max.
[b] Tentative limit Grade No. 1 Fe .02% max.

The following methods are the standard methods used in the laboratories of the New Jersey Zinc Company:

Lead—Electrolytic Method

Solutions Required.—*Silver Nitrate* (*5%*).—Dissolve 5 g. of $AgNO_3$ (C.P.) in 100 ml. of distilled water.

Nitric Acid (*1 : 1*).—Mix 500 ml. of HNO_3 (sp.gr. 1.42) with 500 ml. of distilled water.

Apparatus Required.—*Electrodes.*—The electrodes recommended are of the stationary type.

Anodes.—Platinum cylinder anodes 1.5 inch diameter made from perforated sheets having 288 holes per sq. in.; 2.0 inches high, approximately 20 sq. in. (128 sq. cm.) area with 3.5 inch stem, 0.05 inch diameter. Cylinders must be sand blasted.

Cathodes.—Spiral cathodes each made from a piece of 0.03 inch diameter wire 16 inches long; seven spirals of 0.38 inch diameter extending 2.0 inches with stem of 3.5 inches.

Method.—*Grade No. 1a.*—Weigh 86.6 g. of sample into a 1500-ml. beaker, cover and add 530 ml. of HNO_3 1 : 1 in small portions. When solution is complete, add $AgNO_3$ solution to one drop excess,[21] cover and boil until the volume is about 200 ml.[22] Without cooling, transfer the solution to a 600-ml. beaker and dilute to 500 ml. with cold water. Electrolyze the hot solution,[23] for 4 hours with a current density of 1 ampere per 100 sq. cm. Wash [24] the anode three times with water and dry [25] for 30 minutes at a temperature of 210° C. Cool and weigh. Calculate the percentage of lead as follows:

$$\frac{(A-B)\times 100}{100} = \%\ \text{Pb},$$

where A is the weight of the platinum electrode with deposit of PbO_2, B is the weight of the platinum electrode initially.

Grade No. 1 and 2.—Weigh the sample into a 500-ml. large mouth Erlenmeyer flask, add 75 ml. of water and dissolve with HNO_3 (sp.gr. 1.42). (For Grade No. 1 take 17.32 g. and use 60 ml. of HNO_3. For Grade No. 2 take 8.66 g. and use 40 ml. of HNO_3.) When solution is complete add $AgNO_3$ solution to one drop excess,[21] cover and boil until the volume is about 75 ml.[22] Without cooling, transfer the solution to a tall form 200-ml. beaker, wash out flask with hot water and dilute to 190 ml. Electrolyze the hot solution [23] for 2 hours with a current density of 1 ampere per 100 sq. cm. Wash [24] the anode three times with water and dry [25] for 30 minutes at a temperature of 210° C. Cool and weigh.

Grade No. 3–4–5.—Weigh 17.32 g. of sample into a 500-ml. large mouth Erlenmeyer flask, add 75 ml. of water and 60 ml. of HNO_3 (sp.gr. 1.42) in small portions. When solution is complete add $AgNO_3$ solution to one drop excess,[21] cover and boil until the volume is about 75 ml.[22] Cool, transfer to a 500-ml. graduated flask, and dilute to the mark. Mix and measure out 125 ml. (equal to 4.33 g. of sample) into a tall form 200-ml. beaker. Add 10 ml. of HNO_3 (sp.gr. 1.42) and boil for 10 minutes. Dilute to 190 ml. and electrolyze as directed under Grade No. 1 and 2.

[21] Only sufficient silver nitrate solution is added dropwise to precipitate any chlorides present.

[22] Boiling to this volume with the beaker covered with a watch glass will remove all nitrous fumes. If nitrous acid or similar compounds of nitrogen are not entirely removed, complete deposition of PbO_2 will not be obtained.

[23] After dilution, the solution should be thoroughly mixed by stirring. The temperature should be 70°–80° C. when placed on the stand for electrolysis. During electrolysis the beaker should be covered to prevent loss by spraying.

[24] The washing is best performed by lowering the beaker of electrolyte out from under the electrode and immediately replacing it with a beaker of distilled water. Washing is accomplished by moving the beaker of water up and down several times. This operation is repeated twice with fresh water. The current should be left on until the last washing is finished. The first washing of the electrode should be carried out as soon as possible after the beaker of electrolyte has been removed, since the film of solution which remains on the electrode tends to redissolve the deposit of PbO_2.

[25] Drying at 210° C. for 30 minutes is necessary to remove all but a trace of water from the deposit. The deposit of PbO_2 can be removed from the electrode by immersing in a hot nitric acid solution to which oxalic acid has been added.

The per cent of Pb can be calculated as above directly from the weight of the PbO_2 deposit as factor weights are used in all cases.

Lead Acid Method

Solution Required.—*Lead Acid.*—Add 1 g. of lead acetate in 300 ml. of water to dilute sulfuric acid (300 ml. acid to 1800 ml. of water). Shake well, allow to cool and settle. Filter off the precipitated lead sulfate. By the use of this sulfuric acid saturated with lead, the solubility of lead sulfate need not be considered, the solution being brought back to the same concentration each time.

Method.—Weigh 10 g. of the sample into a 400-ml. beaker and add 120 ml. of "lead acid." When all but about 10% of the zinc is dissolved, filter and wash with lead acid. Retain the filtrate. Wash the metallics back into the beaker and dissolve in nitric acid. Add 40 ml. of "lead acid" and evaporate to strong fumes. Cool and add 35 ml. of water, which is the amount evaporated from the "lead acid," and heat to boiling. Add the filtrate containing most of the zinc and a little lead sulfate, stir and allow to settle over night. Filter on a Gooch crucible, wash with lead acid, a mixture of alcohol and water (1 : 1), finally with alcohol and ignite inside a porcelain crucible and weigh as lead sulfate.

Iron

Solutions Required.—*Sulfuric Acid (1:4).*—Mix cautiously 200 ml. of H_2SO_4 (sp.gr. 1.84) with 800 ml. of cold distilled water.

Copper Sulfate.—Make a saturated solution of copper sulfate in distilled water.

Standard Potassium Permanganate (A).—Dissolve 2.3 g. of $KMnO_4$ (C.P.) in 1000 ml. of boiled distilled water.[26] Mix thoroughly and allow to age at least 14 days and standardize so that 1 ml. shall be equivalent to .004 g. of Fe. This solution should be kept in a dark bottle away from direct light.

Standard Potassium Permanganate (B).—Pipette[27] 50 ml. of Standard Potassium Permanganate Solution (A) into a 500-ml. flask and dilute to the mark with boiled distilled water and mix thoroughly. This solution should be prepared each day it is used.

Apparatus Required.—*Bunsen Valve.*—In a one-hole rubber stopper which will fit the neck of a 500-ml. Erlenmeyer flask insert a short length of glass tubing. Over the upper end of the glass tube place a 2-inch length of soft rubber tubing. Seal the free end of the rubber tubing by inserting a piece of glass rod. In the rubber tubing make a longitudinal slit about ¼" long. When using moisten the slit with water.

Method.—*Grade No. 1a.*—Weigh 100 g. of sample[28] into a 1500-ml. beaker cover, add 400 ml. of HCl (sp.gr. 1.20) and, when the action has nearly stopped,

[26] The $KMnO_4$ is best dissolved in hot water. The solution should be filtered through asbestos and cooled before making up to volume.

[27] The pipette and flask must be standardized; the pipette to deliver one-tenth of the contents of the flask.

[28] Foreign particles of iron contamination in drilled samples should be removed by spreading the sample on a clean, glazed paper and passing a magnet back and forth through the drilling. In the case of samples made from hot metal poured into water the sample should be placed on a 20-mesh clean brass screen and carefully washed with distilled water and dried before weighing.

add 25 ml. of HNO_3 (sp.gr. 1.42). Allow to stand until solution is complete, then boil for 5 minutes. Dilute with 100 ml. of water, neutralize with HN_4OH (sp.gr. 0.90) and add sufficient excess to hold zinc salts in solution. Boil for 5 minutes and allow to stand on a warm plate for 30 minutes. Filter [29] while hot and wash the precipitate twice with hot water. Discard the filtrate. Dissolve the precipitate with hot H_2SO_4 (1 : 4), catching the solution in the original beaker and wash the paper well with hot water. Neutralize with NH_4OH (sp.gr. 0.90) and add 10 ml. in excess. Heat to boiling, filter while hot and wash the precipitate well with hot water. Discard the filtrate. Place a 500-ml. Erlenmeyer flask under the funnel and dissolve the precipitate from the paper with hot H_2SO_4 (1 : 4) and wash well with hot water. Add 5 g. of zinc foil (C.P.), 5–6 drops of $CuSO_4$ solution [30] and stopper immediately with a Bunsen valve. Allow to stand until the zinc foil has dissolved.[31] Filter rapidly through cotton batting into a 500-ml. Erlenmeyer flask. Rinse the first flask with water and wash the funnel and batting.[32] Titrate immediately to a faint pink end point with Standard Potassium Permanganate Solution (B). Make a blank determination in a similar manner. Calculate the percentage of iron as follows:

$$(A-B)\times .0004 = \%\ Fe,$$

where A is the ml. of $KMnO_4$ solution required for the sample; B is the ml. of $KMnO_4$ solution required for the blank.

Other Grades.—Weigh the sample [28] into a 600-ml. beaker, cover, add 150 ml. of water and dissolve in HCl (sp.gr. 1.20). (For Grade No. 1–2–3–4 take 25 g. of sample and use 150 ml. of HCl; for Grade No. 5 take 10 g. of sample and use 60 ml. of HCl.) When solution is complete add 5 ml. of HNO_3 (sp.gr. 1.42), boil for 5 minutes, neutralize with NH_4OH (sp.gr. 0.90) and add sufficient excess to hold the zinc salts in solution. Continue as above. For 25 g. samples multiply the result by 4 and for 10 g. samples by 10.

Standardization.—Weigh 0.15 g. of Bureau of Standards Standard Sample No. 40 Sodium Oxalate into a 400-ml. beaker. Add 200 to 250 ml. of hot water (80°–90° C.) and 25 ml. of H_2SO_4 (1 : 4). Titrate at once with the Potassium Permanganate Solution (A), stirring vigorously, to a permanent pink end point. Adjust the $KMnO_4$ solution so that the end point is reached at 31.25 ml. with 0.15 g. of $Na_2C_2O_4$. One ml. of this solution will be equivalent to .004 g. of Fe.

Cadmium

Solutions Required.—***Sodium Sulfide*** ***(5%)***.—Dissolve 50 g. of NaOH (C.P.) in distilled water, dilute to 1000 ml. and saturate with H_2S gas.

Sulfuric Acid (1 : 5).—Mix cautiously 200 ml. of H_2SO_4 (sp.gr. 1.84) with 1000 ml. of cold distilled water.

Sulfuric Acid (1 : 1).—Mix cautiously 500 ml. of H_2SO_4 (sp.gr. 1.84) with 500 ml. of cold distilled water.

Sulfuric Acid (10%).—Mix cautiously 60 ml. of H_2SO_4 (sp.gr. 1.84) with 1000 ml. of cold distilled water.

[29] Use a No. 40 Whatman 15 cm. filter or other similar paper.
[30] The copper sulfate hastens the action.
[31] This will require from 1 to 2 hours.
[32] Keep the volume 300 ml. for titration.

Hydrochloric Acid (1 : 2).—Mix 500 ml. of HCl (sp.gr. 1.20) with 1000 ml. of distilled water.

Method.—*Grade No. 1a.*—Weigh 200 g. of sample into a 3000-ml. beaker. Add 650 ml. of HCl (sp.gr. 1.20) and after a few minutes carefully add 100 ml. of HNO_3 (sp.gr. 1.42) and boil until solution is complete. Dilute to 1000 ml. with water. Cool in running water and add 1000 ml. of NH_4OH (sp.gr. 0.90) and stir until all zinc salts are in solution.[33] Heat to about 80° C. and add slowly from a pipette 50 ml. of sodium sulfide solution with constant stirring [34] and continue to stir for 5 minutes. Let settle on a warm plate for 30 minutes and filter.[35] Wash beaker once with water. Transfer the paper with precipitate to the 3000-ml. beaker,[36] add 150 ml. of H_2SO_4 (1 : 5), cover and boil gently for several minutes, using a stirring rod to disintegrate the paper and effect solution of zinc and cadmium sulfides.

Filter [37] into a marked 600-ml. beaker [38] and wash well with hot water. Cool, dilute to 400 ml. volume with water and add slowly with constant stirring 25 ml. of sodium sulfide solution and continue stirring for about one minute.[39] Filter [37] and wash out beaker with cold water. Discard the filtrate.

Hold funnel with paper on its side over the marked 600-ml. beaker and wash as much of the precipitate as possible into the beaker with hot H_2SO_4 (1 : 5) using 30–40 ml.[40] Return funnel and beaker to filter stand, open flaps of filter paper and dissolve remaining precipitate with hot H_2SO_4 (1 : 5) using enough to bring the volume to the 60-ml. mark.[41] Stir thoroughly to effect solution of the zinc sulfide and then wash the paper with hot water. Replace the flaps of the filter paper and reserve the funnel with paper for subsequent filtrations.

Dilute the volume to the 250-ml. mark and reprecipitate as before with 25 ml. of sodium sulfide solution. Filter through the reserved funnel and paper and transfer the precipitate to the marked 600-ml. beaker in the manner described in the preceding paragraph.

Make two more precipitations in the same manner.[42] Wash the final pre-

[33] Enough NH_4OH must be added to dissolve all the zinc salts and have considerable in excess.

[34] Stirring briskly is necessary to assure precipitation of all the cadmium.

[35] The time required for filtering may be shortened by using a 15-cm. No. 2 Whatman or similar paper on a 15-cm. Büchner funnel with suction. Refiltering the first 50 to 100 ml. may be necessary.

[36] The small quantity of precipitate adhering to the sides of the Büchner funnel may be washed out into the 3000-ml. beaker with part or all of the 100-ml. of H_2SO_4 (1 : 5) called for in the method.

[37] Use a 15-cm. No. 1 Whatman or similar paper. Most of the lead is removed as $PbSO_4$. The lead remaining is removed subsequently. CuS is insoluble in the H_2SO_4 (1 : 5) and is removed with the lead.

[38] The heights of 60, 250 and 400-ml. volumes should be marked on the 600-ml. beaker. Marking with colored lacquer or paint is quite satisfactory.

[39] Enough zinc sulfide should be precipitated with the cadmium to give a settled layer approximately ¼″ after 10 minutes. When necessary add additional Na_2S solution.

[40] The H_2SO_4 (1 : 5) wash bottle should be equipped with a nozzle which will deliver a fine stream.

[41] It is not essential that all the CdS be dissolved.

[42] The filtrate from the last precipitation should contain no zinc. A simple test is to add 5 ml. of K_4FeCN_6 solution (5%). Another precipitation should be made if the test shows zinc to be present.

cipitate well with cold water and transfer the paper to the 600-ml. beaker, add 30 ml. of H_2SO_4 (1 : 5), cover and boil gently for several minutes, using a stirring rod to disintegrate paper and effect solution of the cadmium sulfide. Dilute to 60 ml. with water, cool and filter into a tall form 200-ml. beaker and wash with cold H_2SO_4 (10%).[43]

Neutralize the filtrate with NH_4OH (sp.gr. 0.90) using methyl orange as indicator.[44] Make the solution slightly acid with H_2SO_4 (10%) and add 5 ml. in excess. Dilute to 150 ml. with water, mix thoroughly, and electrolyze for 3 hours with a current density of one ampere per 100 sq. cm. Wash the cathode with water and alcohol (95%)[45] and dry at 110° C.[46] Cool and weigh.[47]

Calculate the percentage of cadmium as follows:

$$\frac{(A-B)\times 100}{200} = \%\ \text{Cd},$$

where A is the weight of platinum electrode with deposit of cadmium, B is the weight of the platinum electrode initially.

Other Grades.—A sample of 10 (or 25) g. is taken and entirely dissolved in a tall 400-ml. beaker with nitric acid, the solution then treated with 25 (or 50) ml. of H_2SO_4 (1 : 1) and evaporated to expel all nitric acid. After cooling, water is carefully added and the beaker heated until all the soluble salts have been dissolved. The lead sulfate is allowed to settle, filtered off and washed. The filtrate is diluted to 200 ml. and hydrogen sulfide gas passed through for 15–20 minutes. No precipitate will appear at first, so that a drop or two of ammonia is added and repeated at intervals until a considerable amount of zinc sulfide has been precipitated. The sulfides are filtered off and washed with cold water. They are then dissolved with HCl (1 : 2), catching in the original beaker, 15 ml. of H_2SO_4 (1 : 1) added and taken to fumes. This is again diluted to 200 ml., hydrogen sulfide gas passed through and ammonia added as before to produce a precipitate of cadmium sulfide. This is treated as above and a third precipitation made.[42] The final precipitate is dissolved in HCl (1 : 2); 10 ml. of H_2SO_4 (1 : 1) are added and the solution is evaporated to fumes and the cadmium determined electrolytically as directed under Grade No. 1*a*. For 10 g. samples, to determine the percentage of cadmium, multiply the weight of cadmium deposit in grams by 10 and for 25 g. samples multiply by 4.

[43] To remove remaining portion of lead as $PbSO_4$.

[44] Should a white precipitate form, indicating tin, filter through a small paper.

[45] The washing is best performed by lowering the beaker of electrolyte out from under the electrodes and immediately replacing it with a beaker of distilled water. Washing is accomplished by moving the beaker of water up and down several times. This operation is repeated twice with fresh water and once with alcohol. The current must be left on until the last washing is finished. The first washing of the electrodes must be carried out as soon as possible after the beaker of electrolyte has been removed, since the film of the solution which remains on the electrode tends to redissolve the deposit.

[46] Drying should be no longer than necessary to avoid oxidation of the deposit.

[47] Instead of determination by electrolysis, the Cd in the 200-ml. beaker may be precipitated with H_2S gas, filtered on a weighed Gooch crucible, dried at 110° C. and weighed as CdS.

Copper

Solutions Required.—*H_2SO_4 (1 : 1)*.—Mix cautiously 500 ml. of H_2SO_4 (sp.gr. 1.84) with 500 ml. of cold distilled water.

Sodium Thiosulfate (25%).—Dissolve 25 g. of $Na_2S_2O_3 \cdot 5H_2O$ (C.P.) in distilled water and dilute to 100 ml.

Nitric Acid (1 : 4).—Mix 30 ml. of HNO_3 (sp.gr. 1.42) with 120 ml. of distilled water.

Nickel Sulfate Solution.—Dissolve 80 g. of $NiSO_4 \cdot 6H_2O$ in water and dilute to 1000 ml.

Standard Copper Sulfate.—Dissolve .3928 g. of $CuSO_4 \cdot 5H_2O$ (C.P.) in distilled water, add 5 ml. of H_2SO_4 (1 : 1) and dilute to exactly 1000 ml.

Method.—Weigh 100 g. of sample into a 2000-ml. beaker. Add 1000 ml. of H_2O, 25 ml. of nickel sulfate solution [48] and 225 ml. of H_2SO_4 (1 : 1). After all the zinc has been dissolved, heat the solution to boiling and add 10 ml. of sodium thiosulfate solution (25%). Boil until precipitate coagulates, let settle a few minutes. Filter [49] and wash thoroughly with cold water.

Transfer the paper and precipitate to the original beaker, add 50 ml. of HNO_3 (1 : 4) and boil gently for several minutes using a stirring rod to disintegrate the paper and effect solution of the copper sulfide. Filter [50] into a 250-ml. beaker and wash well with hot water. Discard the paper.

Add 10 ml. of H_2SO_4 (1 : 1), evaporate to strong fumes, destroy the organic matter by adding HNO_3 (sp.gr. 1.42) dropwise to the hot acid solution and take to complete dryness over a Meker burner.

Take up in a few drops of H_2SO_4 (1 : 1) and 10 ml. water. Heat to boiling, cool, filter [51] into a 50-ml. beaker and wash filter well with cold water. Discard the paper.

Reduce the volume of the filtrate to 2 to 3 ml. by boiling, neutralize [52] with NH_4OH (sp.gr. 0.90) and add 2 ml. excess. Heat to boiling and filter, catching the filtrate in a small flat bottom color comparison tube, and wash with five 1-ml. increments of cold water. (Volume in comparison tube should not exceed 10 ml.)

Make a standard copper solution for comparison in a similar comparison tube as follows:

Add 2 drops H_2SO_4 (1 : 1) to 3 ml. water, neutralize with NH_4OH (sp.gr. 0.90) and add 2 ml. in excess. Then add standard copper solution from a burette [53] until the blue color matches the color in the tube containing the copper from the sample when diluted to the same volume.[54]

[48] Nickel sulfate accelerates the action so that care must be used not to add the H_2SO_4 too rapidly.

[49] Use a No. 2 Whatman 15-cm. filter or similar paper.

[50] Use a No. 1 Whatman 12.5 filter or similar paper.

[51] Use a No. 2 Whatman, 15-cm. filter or similar paper. The lead is separated in this filtration.

[52] Use litmus paper as the indicator.

[53] Additions of 1-ml. increments are recommended.

[54] If the sample contains more than .001% Cu a smaller sample should be used or an aliquot of the final solution may be taken. Samples containing over .01% Cu should be completed electrolytically as described under Standardization of Standard Copper Sulfate Solution.

Calculate the percentage of copper as follows:

$$\frac{(A-B)\times .0001\times 100}{100}=\%\ \mathrm{Cu},$$

where A is the number of ml. of the standard copper solution required to equal the color of the sample, B is the number of ml. of the standard copper solution required to equal the color, if any, obtained by a blank determination, i.e. carrying all quantities of reagents and water through the procedure. 0.0001 is the weight in grams of copper per ml. of standard copper solution.

Standardization of the Copper Sulfate Solution

Method.—Measure 100 ml. of the copper sulfate solution into a tall form 200-ml. beaker and add 2 ml. of HNO_3 (sp.gr. 1.42) and 10 ml. of H_2SO_4 (1 : 1). Dilute to 150 ml. with water and electrolyze for 3 hours with a current density of one ampere per 100 sq. cm. Wash the cathode with water,[55] then with alcohol (95%) and dry at 110° C.[56] in an oven. Cool and weigh.[57]

Calculate the grams of copper per ml. as follows:

$$\frac{A-B}{100}=\text{g. Cu per ml.},$$

where A is the weight of platinum electrode with deposit of copper, B is the weight of platinum electrode initially.

ZINC IN METALLIC CADMIUM

Solutions Required.—*Sulfuric Acid (1:1).*—Mix cautiously 200 ml. of H_2SO_4 (sp.gr. 1.84) with 200 ml. of cold distilled water.

Hydrochloric Acid (1 : 2)—Mix 300 ml. of HCl (sp.gr. 1.20) with 600 ml. of distilled water.

Method.—Weigh 10 g. of sample into an 800-ml. beaker, add 200 ml. of water, cover beaker and add 25 ml. of HNO_3 (sp.gr. 1.42). When action has ceased, add 15 ml. of H_2SO_4 (1 : 1), remove cover and evaporate to complete dryness. Cool, add 200 ml. of water and 40 ml. of H_2SO_4 (1 : 1), cover, bring to a boil slowly [58] and boil until all soluble salts are dissolved. Cool, make the volume 400 ml., and pass a rapid stream of H_2S gas through the solution for 15 min-

[55] The washing is best performed by lowering the beaker of electrolyte out from under the electrodes and immediately replacing it with a beaker of distilled water. Washing is accomplished by moving the beaker of water up and down several times. This operation is repeated twice with fresh water and once with alcohol. The current must be left on until the last washing is finished. The first washing of the electrodes must be carried out as soon as possible after the beaker of electrolyte has been removed, since the film of the solution which remains on the electrode tends to redissolve the deposit.

[56] Drying should be no longer than necessary to avoid oxidation of the deposit.

[57] The weight of copper sulfate taken should make a solution which will contain 0.0001 g. copper per 1 ml. If this strength is not obtained, adjust the solution and re-standardize as above.

[58] The residue cake might crack the beaker if heated too strongly at first. It is well to break up the residue with a glass stirring rod before heating.

utes.[59] Allow to settle, and filter,[60] catching the filtrate in an 800-ml. beaker. Wash the precipitate once by decantation with water and transfer the precipitate to the paper. Permit to drain, then remove the beaker containing filtrate and place it on warm plate to evaporate.

Place beaker, in which the precipitation was made, under funnel and dissolve the precipitate into the beaker by washing with HCl (1 : 2) washing finally with cold water. Add 15 ml. of H_2SO_4 (1 : 1) to the solution and evaporate to complete dryness. Cool, add 200 ml. of water and 40 ml. of H_2SO_4 (1 : 1), cover, bring to a boil slowly [58] and boil until all soluble salts are dissolved. Cool, make the volume 400 ml. and pass a rapid stream of H_2S gas through the solution for 15 minutes.[59] Filter,[60] washing the precipitate once on the paper. Discard the paper and precipitate. Add this filtrate to that previously obtained.

Evaporate the combined filtrates to complete dryness. Cool, add 100 ml. of water and 25 ml. of H_2SO_4 (1 : 1), heat to boiling, and boil until the soluble salts are dissolved. Cool, make the volume 400 ml. and pass a rapid stream of H_2S gas through the solution for 15 minutes. Filter,[61] catching the filtrate in a 600-ml. beaker and washing with cold water. Evaporate to complete dryness. Add 3 ml. of HCl (sp.gr. 1.20) and 20 ml. of water and heat until solution is complete. Cool and wash into a 100-ml. Nessler tube and estimate the zinc by the turbidimetric method as described under "Determination of Small Amounts of Zinc."

ANALYSIS OF ZINC CHLORIDE SOLUTION [62]

The methods to be used for the analysis of zinc chloride solution or fused zinc chloride are essentially those given under the various chapters for the various elements. It seems advisable, however, to include a set of methods of analysis suitable for the commercial evaluation of zinc chloride.

Specific Gravity at 15° C.

The specific gravity is determined by means of a picnometer. The volume is brought to the graduation after the solution in the picnometer has been brought to 15° C., using a water bath. The weight of this volume of boiled distilled water is determined at 15° C., and the specific gravity of the zinc chloride solution calculated, compared to water at 15° C.

Zinc (Manganese and Copper Absent)

About 25 grams of the well shaken solution is weighed out in a weighing bottle and transferred to a 500 ml. graduated flask. Sufficient nitric acid is added to clarify the solution upon dilution. The flask is filled to the mark with distilled water and thoroughly mixed.

[59] To precipitate the bulk of the cadmium as CdS.

[60] Use a 15-cm. qualitative paper. This is a rough separation. Any CdS which goes through the paper will be removed later.

[61] Use a close 11-cm. paper. This is the final removal of the last traces of cadmium.

[62] Contributed by L. S. Holstein and L. A. Wilson.

A portion, approximately equivalent to one gram of $ZnCl_2$ is accurately measured from a pipette or a burette and the zinc determined by titration with a standard potassium ferrocyanide solution as given under procedure for zinc in ores.

Zinc (Manganese or Copper Present)

If manganese or copper is present an aliquot portion is measured out and the manganese or copper separated according to the methods given under procedures for ores, before titration with potassium ferrocyanide.

Chlorine

Another portion of this solution, approximately equivalent to 0.5 gram of $ZnCl_2$ is measured off into a 500 ml. Erlenmeyer flask; 15 ml. of distilled water, 100 ml. of standard N/10 silver nitrate solution and 40 ml. of nitric acid are added to the flask and boiled until all nitrous fumes are driven off. After cooling, the excess silver nitrate is titrated with standard N/10 ammonium thiocyanate solution using 5 ml. of (1:6) ferric nitrate solution as an indicator. A blank is run at the same time and the amount of chlorine determined from the difference in volumes of ammonium thiocyanate required. The factor for the standard ammonium thiocyanate solution is best determined with C.P. sodium chloride.

Sulfuric Anhydride (SO_3)

Twenty-five ml. of the original well shaken solution of zinc chloride are measured off with a pipette into a 400 ml. beaker, diluted to 300 ml. with hot water and a few drops of hydrochloric acid added. Any insoluble matter is filtered off, 5 ml. of bromine water are added to the filtrate and the solution boiled until excess bromine is all driven off. The SO_3 in the filtrate is precipitated with 25 ml. of hot 10% barium chloride solution. After standing on the steam plate for 3 hrs., the barium sulfate is filtered off, ignited and weighed. The weight of the sample is determined from the specific gravity.

Iron (Fe)

A portion of the well shaken solution, equivalent to 10 grams of zinc is evaporated to a syrupy consistency and the iron determined by the colorimetric method as under spelter.

In case the iron is too high to estimate colorimetrically it is separated with ammonia, filtered off, washed with hot water and dissolved in hot dilute sulfuric acid. This solution is cooled, run through a Jones reductor and titrated with standard potassium permanganate solution, or the iron may be determined by the hydrogen sulfide method as given under analysis of slab zinc.

Iron and Aluminum ($Fe_2O_3+Al_2O_3$)

Either 10 or 20 ml. of the original well shaken solution are transferred to a 200 ml. beaker, diluted with 150 ml. of water and hydrochloric acid added to a very faint excess (2 drops concentrated acid). A rapid stream of hydrogen sulfide is passed through the solution for 30 to 40 minutes. The precipitate of zinc sulfide is filtered off and washed thoroughly. The filtrate is boiled for

about 15 minutes to remove hydrogen sulfide, cooled, sufficient bromine water added to more than oxidize all the iron, and then boiled to remove the excess bromine. Ammonium hydroxide is now added in slight excess, the precipitate of iron and alumina filtered off and washed with hot water. The precipitate is dissolved from the paper with hot hydrochloric acid (1 : 4) re-precipitated, filtered off, washed free from chlorides, ignited and weighed.

Manganese (Mn)

Either 10 or 20 ml. of the original well shaken solution are transferred to a 400 ml. beaker, 25 ml. of sulfuric acid (1 : 1) added and evaporated to practically complete expulsion of all excess sulfuric acid. Nitric acid (1 : 3) is now added and the manganese determined according to the bismuthate method.

Lime (CaO)

Twenty-five ml. of the well shaken solution are measured off with a pipette, a few drops of hydrochloric acid added, and the solution diluted to 150 ml. Twenty grams of ammonium chloride and a few drops of bromine water are added. The iron and manganese are precipitated by ammonia and filtered off after bringing to boiling. The filtrate is evaporated to 150 ml., the lime precipitated with 25 ml. of ammonium oxalate solution (saturated solution) and allowed to stand for 3 hours. The calcium oxalate is filtered off and washed four times with hot water. A hole is then punched in the filter paper, the precipitate washed into a 400 ml. beaker with boiling water, 10 ml. of sulfuric acid (1 : 1) poured over the paper and the paper washed with boiling water. The solution is diluted to 150 ml. with hot water and titrated with standard potassium permanganate solution.

Magnesia (MgO)

The filtrate and washings from the lime determination is made slightly acid with hydrochloric acid and 15 ml. of a saturated solution of microcosmic salts added. The solution is cooled and the magnesia precipitated by the slow addition of ammonia. Sufficient ammonia must be added to hold all zinc in solution, an excess of about 50 ml. being required. The precipitate after standing 12 hours is filtered off, and redissolved in hot 1 : 4 hydrochloric acid. Twenty grams of ammonium chloride are added to this solution, then a few drops of microcosmic solution, and precipitation effected with ammonia as before, the excess of ammonia being only 10 ml. in this case. After standing 12 hours, the precipitate is filtered off, washed six times with 1 : 10 ammonia water, or until free from chlorides, ignited and weighed as $Mg_2P_2O_7$.

Alkalies (NaCl+KCl)

A sample of about 10 grams is taken and made up to a volume of 500 ml. From this a portion equivalent to approximately 2 grams is measured off, slightly acidified with hydrochloric acid and the zinc precipitated with hydrogen sulfide. After filtering, the filtrate is made slightly alkaline with ammonia and tested with a small amount of ammonium sulfide, and any zinc, iron and manganese precipitated is filtered off. The filtrate is acidified with HCl and boiled

for about thirty minutes to drive off the hydrogen sulfide. A small amount of bromine water is added and the boiling continued until the excess of bromine has been removed. The solution is diluted to about 200 ml. with hot water, and 10 ml. of hot 10% $BaCl_2$ solution added, to precipitate SO_3. Without filtering off the barium sulfate, the solution is made ammoniacal, one gram of ammonium carbonate and 5 ml. of ammonium oxalate solution added and the precipitates allowed to settle in a warm place. The precipitate is filtered off, washed with hot water, and the combined filtrate and washings evaporated to dryness in a porcelain dish. The ammonium salts are completely driven off by ignition over a low flame. The residue remaining is dissolved in a small amount of water with two drops of hydrochloric acid, transferred to a weighed platinum dish, the porcelain dish being washed with a minimum amount of water, evaporated to dryness on a hot plate, and after cooling weighed.

Any magnesia which may be present with the alkali chlorides is determined, calculated to $MgCl_2$ and deducted from the weight of the salts in the dish. This difference is expressed as combined alkali chlorides $KCl+NaCl$.

Copper

Twenty ml. of solution are taken, 5 grams of ammonium chloride, and 20 ml. of ammonium hydroxide added, diluted to 100 ml. in a color comparison tube and compared with a zinc chloride solution of equal strength, to which a measured amount of standard copper solution is added to give the same depth of color. If iron interferes with the color comparison, it should be filtered off before diluting to volume. When the color of copper present is over 0.05%, the determination should be carried out by some other method. See chapter on Copper.

Barium (Ba)

If sulfuric anhydride (SO_3) is found to be present, it is not worth while to make a determination for barium. If no sulfuric anhydride is present, barium should be looked for and determined by diluting 10–20 ml. to 300 ml. with water, adding slight excess of hydrochloric acid heating to boiling and precipitating the barium with ammonium sulfate solution 10%.

ANALYSIS OF FUSED ZINC CHLORIDE

The analysis of fused zinc chloride for zinc, etc., is carried out by the same methods as given under Zinc Chloride Solution, working on a solution of the fused salt in water. This solution is made up by rapidly transferring approximately 20 grams of fused salt to a weighing bottle, weighing, dissolving in water in a 2000 ml. graduated flask to which a few drops of nitric acid has been added to prevent precipitation of basic zinc chloride, and filling to the mark. Aliquot portions are taken from this solution for the various determinations.

Special determinations are sometimes called for with fused zinc chloride which is to be used for some special purpose. It is very essential that such analyses be carried out carefully according to the method prescribed in order that the results, which are largely empirical, may be comparable. One analysis

of this sort which is commonly called for is Basicity expressed in some empirical way to give a measure of the relative quantities of the basic zinc chloride, which will settle out upon dissolving fused zinc chloride in water. It may be expressed as the volume of standard hydrochloric acid (usually N/2) required to neutralize 10 ml. of a 40° Baume solution of the fused zinc chloride, diluted with 300 ml. of water, when using methyl orange as indicator, or the weight of basic chloride obtained by treating 10 grams of the sample, weighed in a weighing bottle, with 400 ml. of water, agitating to complete all possible solution, filtering off insoluble on a Gooch crucible and washing with water until combined filtrate and washings total just 1000 ml.

Ammonia (NH_3)

It is often of value to know if ammonium chloride is present. A sample of 5–10 grams is weighed and transferred to a 500 ml. distilling flask, 100 ml. of water, 50 ml. of sodium hydroxide (20%) and a small quantity of granulated zinc added.[63] The ammonia and water are distilled over into an absorption bottle containing a measured quantity of standard acid. The excess of acid is titrated with standard alkali solution, using methyl orange.

See chapter on Nitrogen, page 629, also Analysis of Paint Pigments, Volume II.

DETERMINATION OF ZINC IN PIG LEAD

A.S.T.M. Methods

Solutions Required.—*Nitric Acid (1 : 4).*—Mix 200 ml. of HNO_3 (sp.gr. 1.42) with 800 ml. of distilled water.

Sulfuric Acid (1 : 1).—Carefully pour, with stirring, 500 ml. of H_2SO_4 (sp.gr. 1.84) into 500 ml. of distilled water.

Acidulated Hydrogen Sulfide Water.—Add 20 ml. of HCl (sp.gr. 1.19) to 1000 ml. of distilled water and saturate with hydrogen sulfide.

Ammonium Thiocyanate Solution (2%).—Dissolve 20 g. of NH_4CNS in 1000 ml. of distilled water.

Hydrochloric Acid (1 : 3).—Mix 100 ml. of HCl (sp.gr. 1.19) and 300 ml. of distilled water.

Standard Zinc Solution (0.1 mg. of zinc per ml.).—Dissolve exactly 0.1 g. of U. S. Bureau of Standards pure zinc in 5 ml. of HCl (sp.gr. 1.19) and dilute to exactly 1000 ml. of distilled water.

Potassium Ferrocyanide Solution.—Dissolve 34.8 of $K_4Fe(CN)_6 \cdot 3H_2O$ in 1000 ml. of distilled water.

Method.—Dissolve 222.23 g. of the sample in 1100 ml. of HNO_3 (1 : 4), using a 1300 ml. beaker. When the lead is dissolved, transfer the solution to a 2000 ml. graduated flask and add slowly 150 ml. of H_2SO_4 (1 : 1). Cool, fill the flask to the mark and then pour the solution into a clean 3000 ml. flask provided with a rubber stopper. Rinse the measuring flask with exactly 50 ml. of water, which is equivalent to the volume of lead sulfate which is present. Mix the solution thoroughly by shaking, allow the precipitate to settle and filter through a dry filter until 1800 ml. of filtrate has been obtained.

[63] The addition of granulated zinc aids in the expulsion of the ammonia by hydrogen formed with the sodium hydroxide.

Place exactly 1800 ml. of filtrate (equivalent to a 200-g. charge) in a No. 9 porcelain evaporating dish and evaporate the solution to approximately 100 ml. Transfer the solution to a 600 ml. beaker, neutralize with ammonia, and then add 5 ml. of HCl (sp.gr. 1.19) for every 100 ml. of solution. Warm the solution and pass in a rapid current of hydrogen sulfide until it is saturated. Digest for 30 minutes on the steam bath, add an equal volume of water and again saturate with hydrogen sulfide. Filter and wash with acidulated H_2S water.

Discard the precipitate and evaporate the filtrate in glassware containing no zinc (such as Pyrex) until the volume of the solution is approximately 100 ml.

Neutralize the solution with ammonium hydroxide, add 5 g. of citric acid, and warm until the acid is dissolved. Add small portions of calcium carbonate to the hot citric acid solution until about 1 g. of calcium citrate has separated and then pass in a rapid current of H_2S as the solution is allowed to cool. Allow the solution to stand for from 2 to 4 hours, part of the time on a water bath, until the supernatant liquid is clear.

Collect the precipitate on a filter, wash with a 2% solution of ammonium thiocyanate and then dissolve the precipitate in hot dilute hydrochloric acid (1 : 3). If the solution has a reddish color (due to iron), the zinc must be reprecipitated as above. If the solution is clear, evaporate it to dryness on the steam bath, take up the residue in 3 ml. of HCl (sp.gr. 1.19), add 20 ml. of water and filter if not perfectly clear.

Transfer the solution (Note 2) to a 50 ml. Nessler jar and dilute to 45 ml. Prepare other Nessler jars containing 3 ml. of HCl (sp.gr. 1.19), definite volumes of standard zinc solution, and diluted to 45 ml. Add 5 ml. of potassium ferrocyanide solution to each jar, mix quickly, and compare the turbidities by viewing longitudinally as the jars are held over a sheet of fine print. Add more of the standard zinc solution from a burette to the jar which approximates the turbidity of the unknown most closely, until the turbidities match each other, and calculate the percentage of zinc on the basis of a 200-g. sample or the aliquot portion taken.

Notes.—1. All glassware that contains zinc must be avoided and in umpire work a blank test should be carried along with the test.

2. The whole solution can be used if the lead contains no more than 0.002% of zinc. If more zinc is present, it is best to take such an aliquot portion of the solution as will give approximately 4 mg. of zinc and then to add enough HCl to provide 3 ml.

3. For further details concerning the turbidmetric test, consult the "Determination of Small Quantities of Zinc" by M. Bodansky, J. Ind. Eng. Chem., 13, 696–697 (1921).

4. The addition of calcium carbonate with the formation of a precipitate of calcium citrate serves the purpose of giving a clear filtrate, and prevents the loss of colloidal sulfide.

ZINC IN BRASS

The sample is dissolved in HNO_3 and HCl and evaporated to dryness. It is now treated with 2.5 ml. of HCl or 1.5 ml. of H_2SO_4 and 50 ml. of water and saturated with H_2S, then diluted to 100 ml. and again saturated with H_2S. Copper sulfide, etc., are filtered off and washed to recover occluded zinc. The filtrate containing the zinc is neutralized with ammonia added dropwise after expelling the H_2S by boiling. The zinc is now determined gravimetrically as $Zn_2P_2O_7$ by

precipitation from the neutral solution with $(NH_4)_2HPO_4$ as described under "Gravimetric Methods," or precipitated as ZnS in a slightly acid solution and determined volumetrically by titrating with standard potassium ferrocyanide solution as described under "Standard Method."

DETERMINATION OF ZINC IN RUBBER GOODS

Ferrocyanide Method

Carefully ash a two gram sample of the rubber keeping the temperature low to prevent reduction and volatilization of zinc. Dissolve the ash in 15 ml. of hydrochloric acid (sp.gr. 1.19) in a 250-ml. beaker. Remove the crucible, wash thoroughly with a minimum amount of hot water, and boil down to 5 ml. volume. Cool, and wash down sides of beaker. Add 10 ml. of saturated bromine water, 5 grams of ammonium chloride, 15 ml. of NH_4OH (sp.gr. 0.90), and boil vigorously for three minutes.

Filter off the precipitated hydroxides and insoluble material, and wash four times with 100 ml. of hot water, in 25 ml. portions, containing 50 grams of NH_4Cl and 25 ml. of NH_4OH (sp.gr. 0.90) per liter. Dilute the solution to 200 ml., heat to boiling, and add 4 drops of a concentrated ammonium sulfide solution to destroy oxidizing agents. Carefully neutralize with hydrochloric acid (sp.gr. 1.19) using litmus paper as an indicator and add 3 ml. excess. Titrate with standard potassium ferrocyanide solution as directed under "Titration in Acid Solution with Outside Indicator."

Interfering elements such as manganese, copper, cadmium, etc., are rarely used in rubber compounds.

DETERMINATION OF ZINC IN SOLDER[64]

Solutions Required.—*Mixed Acid.*—Dissolve 20 g. of NH_4Cl in 500 ml. of distilled water, add 400 ml. of HCl (sp.gr. 1.19), mix and add 100 ml. of HNO_3 (sp.gr. 1.42).

Dilute Hydrochloric Acid for Dilution.—To 500 ml. of cold distilled water, add 10 ml. of HCl (sp.gr. 1.19) and pass H_2S for 15 minutes.

Citric Acid Solution.—Dissolve 250 g. of $H_3C_6H_5O_7 \cdot H_2O$ in 500 ml. of distilled water.

Ammonium Thiocyanate Wash Solution.—Dissolve 20 g. of NH_4CNS in 1000 ml. of distilled water and filter through a dry paper.

Standard Zinc Solution.—Dissolve exactly 0.1 g. of U. S. Bureau of Standards pure zinc in 10 ml. of HCl (sp.gr. 1.19) and dilute to exactly 1000 ml. with distilled water.

Potassium Ferrocyanide Solution.—Dissolve 21.54 g. of $K_4Fe(CN)_6 \cdot 3H_2O$ in about 800 ml. of distilled water. When dissolved dilute to 1000 ml. with distilled water and mix.

Method.[65]—Weigh 6.25 g. of the sawings, free from metallic iron, into a 250-ml. beaker, add 150 ml. of the mixed acid and heat over a low flame on

[64] Standard Method by the National Lead Company through kindness of W. J. Brown.

[65] See "Determination of Small Quantities of Zinc," by M. Bodansky. J. Ind. Eng. Chem., **13**, 696 (1921).

the hot plate. When $PbCl_2$ begins to form, decant the clear solution into a 400-ml. beaker, again add 150 ml. of the mixed acid to the undissolved alloy and continue heating until solution is complete. Two 150-ml. additions of the mixed acid should suffice to completely dissolve the alloy without the formation of appreciable $PbCl_2$ in the hot solution. When completely dissolved, combine the two solutions and evaporate down to a volume of about 75 ml. Allow to stand in the cold over night. Separate the $PbCl_2$ by decantation, washing three times with cold HCl (1 :2) into a 600-ml. beaker. Discard the residue. Evaporate the solution nearly to dryness, add 10 ml. of HCl (sp.gr. 1.19), dilute with 100 ml. of water, bring to boiling and pass H_2S through the solution. As the sulfides precipitate gradually dilute with hot distilled water until a volume of 300 ml. is attained and continue passing H_2S for 30 minutes. Transfer to a 500-ml. graduated flask, cool to room temperature, make up to the mark with " dilute hydrochloric acid for dilution," and mix. Filter off 400 ml. through a dry filter, discarding the first 20 ml. of the solution. Transfer the filtered solution to a 600-ml. beaker,[66] add 5 ml. of H_2SO_4 (sp.gr. 1.84), evaporate to fumes, cool, add 50 ml. of distilled water, bring to boiling, allow to stand in the cold for an hour or so, filter and wash with dilute H_2SO_4 (1 : 9). Discard the residue. Bring the filtrate to boiling, add 3 or 4 ml. of HNO_3 (sp.gr. 1.42) to oxidize iron, make strongly alkaline with NH_4OH, again bring to boiling and allow to stand in a warm place an hour or so for the iron to completely precipitate. Filter and wash into a 600-ml. beaker.

Boil the filtrate to expel NH_4OH, add 10 ml. of the citric acid solution, dilute to a volume of 350 ml., again bring to boiling, and add, a little at a time, solid $CaCO_3$ [67] until about 1 g. of calcium citrate separates. Pass H_2S through the solution until cold and allow to stand several hours, part of the time on a water bath. Filter and wash with the NH_4CNS wash solution.

Wash the precipitate back into the beaker with as little water as possible and set under the funnel. Now pour through the filtrate 10–15 ml. of hot HCl (1 : 1) and replace the beaker with a 100-ml. graduated flask. Bring the solution in the beaker to boiling and filter through the same filter. Wash several times with hot distilled water. Cool the solution in the flask to room temperature, make up to the mark with distilled water at room temperature and mix. Reserve as solution No. 1. At the same time the sample is being run a " blank " should be carried along. The solution on the blank in another 100 ml.-graduated flask should be reserved as solution No. 2.

Pipette off 25 ml. of solution No. 1 into a 100-ml. Nessler tube, add 2 ml. of the $K_4Fe(CN)_6$ solution, make up to the mark with distilled water and shake well. Into another 100-ml. Nessler tube, pipette 25 ml. of solution No. 2, add 2 ml. of $K_4Fe(CN)_6$ solution, make up to the mark with distilled water, mix and add the standard zinc solution a few drops at a time until the turbidities match. Shake well between each addition of the standard. Before the final comparison is made both solutions No. 1 and No. 2 should stand about 5 minutes to allow the maximum turbidity to develop.

[66] It might be expedient at this stage to pass H_2S through the solution to ascertain if all the tin has been precipitated. If a precipitate forms, filter and wash with "dilute HCl for dilution."

[67] When $CaCO_3$ is added to the hot solution violent frothing takes place. Unless extreme care is taken in adding the $CaCO_3$, the determination may be spoiled.

Comparison is best made by setting the tubes over a sheet of fine print and looking down the tubes.

DETERMINATION OF ZINC COATING ON GALVANIZED SHEETS AND WIRE (A.S.T.M. METHODS)

Galvanized Sheets

Spot Test Method

Sampling.—Section 5.

(*a*) All specimens shall be exactly 2¼ in. square (57.2 mm. square). The weight of coating in g. on a piece 2¼ in. square (5.06 sq. in.) (3277 sq. mm.) is numerically equal to the weight of coating in ounces per square foot of sheet.

(*b*) Three specimens for the triple spot test shall be taken from each test sheet, one from the center and the other two from diagonally opposite corners but at least 4 in. (100 mm.) from the end and 2 in. (50 mm.) from the side of the sheet.

(*c*) The specimen for the minimum spot test shall be either that one of the three specimens of the triple spot test bearing the lightest coating or, a single specimen taken from any part of the sheet at least 4 in. (100 mm.) from the end and 2 in. (50 mm.) from the side of the sheet.

(*d*) The specimens shall be clean; if necessary, they shall be washed with solvent naphtha or other suitable solvent, then with alcohol, and dried thoroughly.

Reagents Required.—Section 6.

Antimony Chloride Solution.—Dissolve 20 g. of antimony trioxide or 32 g. of $SbCl_3$ in 1000 ml. of HCl (sp.gr. 1.19).

Hydrochloric Acid.—Concentrated HCl (sp.gr. 1.19).

Procedure.—Section 7.

(*a*) ***Triple Spot Test.***—The three 2¼ in. square specimens, obtained in accordance with Section 5 (*a*), (*b*) and (*d*), shall be weighed together, except as specified in Paragraph (*b*), to the nearest 0.01 g. After weighing, each specimen shall be immersed singly in a solution, made by adding 5 ml. of antimony chloride solution to 100 ml. of HCl (sp.gr. 1.19), and allowed to remain therein until the evolution of hydrogen has ceased or until only a few bubbles are being evolved. This requires only about 15 to 30 seconds, except in the case of sherardized coatings which require a somewhat longer time. The same solution may be repeatedly used, without further additions of antimony chloride solution, until the time required for stripping becomes inconveniently long. The temperature of the stripping solution shall at no time exceed 100° F. (38° C.). After stripping, the specimens shall be washed and scrubbed under running water, dried first with a towel and then by heating to about 212° .F (100° C.), and cooled. The specimens shall then be again weighed together to the nearest 0.01 g. The loss of weight in g. divided by the number of specimens represents the weight of coating in g., which is numerically equal to the weight of coating in ounces per square foot of sheet. Results shall be reported to two decimal places.

(*b*) ***Minimum Spot Test.***—If it is desired to select for the minimum spot test that one of the three specimens of the triple spot test bearing the lightest

coating, the procedure shall be the same as described in Paragraph (*a*), except that each of the three specimens shall be weighed individually instead of collectively. If the individual specimen obtained in accordance with Section 5 (*c*) is selected for this test the procedure shall be the same as described in Section 7 (*a*).

Galvanized Wire

Stripping Test

Sampling.—Section 11.

For determining the weight of coating on zinc-coated (galvanized) wire, the use of a test specimen of a specific length is not necessary; since the density of the steel (0.283 lb. per cu. in.) is known, it is only required to determine the diameter of the stripped wire and the ratio of the weight of zinc to the weight of the stripped wire. The specimen of galvanized wire may be of any length over 12 in. but preferably about 24 in.

Procedure.—Section 13.

(*a*) The test specimen shall be cleaned with solvent naphtha or other suitable solvent, then with alcohol, and dried thoroughly, and then weighed to the nearest 0.01 g. If the vessel to be used for the stripping bath is of small size, the specimen shall be loosely coiled to facilitate complete immersion.

(*b*) The specimen shall then be stripped of the zinc coating by complete immersion in any convenient volume of solution made by adding 5 ml. of antimony chloride solution to each 100 ml. of concentrated HCl. The same solution may be repeatedly used, and without further additions of antimony chloride solution, until the time required for stripping becomes inconveniently long. The temperature of the stripping solution shall at no time exceed 100° F. (38° C.).

(*c*) The number of specimens immersed at any one time shall not exceed three per 100 ml. of solution. For single determinations a convenient volume of solution is 100 ml. in a glass cylinder 2 in. in diameter and 6 in. in depth. As soon as the violent chemical action on the wire has ceased, the wire shall be removed from the acid, washed thoroughly and wiped dry. The diameter of the wire shall then be determined to the nearest 0.001 in. by taking the average of two measurements at right angles to each other. The stripped sample shall then be weighed to the nearest 0.01 g.

Calculation.—Section 14.

The original weight minus the weight of the stripped specimen, divided by the weight of the stripped specimen, gives the ratio of zinc to iron for the specimen under test. The weight of coating in ounces per square foot of stripped wire surface is determined by multiplying the constant 163 by the diameter in inches of the stripped wire by the above ratio. This calculation may be expressed by the following formula:

$$\text{Ounces of zinc per square foot of stripped wire surface} = 163dr,$$

where

$$d = \text{the diameter in inches of stripped wire};$$

and

$$r = \frac{\text{original weight} - \text{stripped weight}}{\text{stripped weight}}$$

TENTATIVE METHOD OF TEST FOR QUANTITATIVE SPECTROCHEMICAL ANALYSIS OF ZINC FOR LEAD, IRON AND CADMIUM [68]

A.S.T.M. Designation: E 26–35 T [69]

Scope.—1. This method [70] may be applied to any grade of zinc providing the lead, iron and cadmium content are less than 0.1%. An arc spectrum is used, employing graphite electrodes, one of which is treated with a solution of the sample to be analyzed. Quantitative estimations are made by the comparison of the spectrum of the sample being analyzed with the spectra of standard samples of known composition.

Preparation of Sample Solution.—2. A 20-g. portion of a representative sample of the zinc to be analyzed shall be weighed, placed in a 250-ml. beaker and dissolved in hydrochloric acid (Note 1). If the volume of the solution is greater than 35 ml., it shall be evaporated to approximately 35 ml., cooled, transferred to a 50-ml. graduate, distilled water added to bring the volume to 40 ml. and the solution transferred to a small glass-stoppered bottle. This procedure shall be repeated, thus making available duplicate sample solutions.

Preparation of Electrode.—3. A 0.1 ml. of one of the sample solutions shall be introduced into a recessed graphite electrode (Note 2). Directly after the introduction of the solution, the electrode shall be dried in an oven at 200° F. (93° C.) for about 30 min.

Preliminary Estimation.—4. (*a*) The electrode containing the sample solution shall be made the lower and positive member of a pair of electrodes between which an electric arc shall be created by applying a potential of 80 to 100 v. with a direct current of 10 amp. The spectrum of the arc shall be recorded (Note 3) by means of a spectrograph from the moment the arc is struck until the arc has burned for 2 min. The plate thus obtained shall be referred to as the preliminary plate.

(*b*) The preliminary plate shall be compared with a standard plate (Note 4) on which are recorded the spectra of the standard solutions (Note 5). By visual comparison of the blackness of the spectral lines (Note 6) of lead, iron and cadmium in the spectrum of the sample with the corresponding lines in the standard spectra, the approximate impurity content of the sample shall be ascertained.

Final Estimation.—5. (*a*) The final estimation of the impurity content shall be made on the basis of plates on each of which are photographed two spectral exposures of the sample and three standard spectral exposures. Beginning with one impurity, for example, lead, three standards of various lead contents, a high, a medium and a low content, respectively, shall be selected.

[68] Under the standardization procedure of the Society, this method is under the jurisdiction of the A. S. T. M. Committee E-2 on Spectrographic Analysis.

[69] This is a Tentative Standard and under the Regulations of the Society is subject to annual revision. Suggestions for revision should be addressed to the Headquarters of the Society, 260 S. Broad St., Philadelphia, Pa. Issued, 1935. Accepted for publication as tentative by Committee E-10 on Standards, October 7, 1935.

[70] The procedure is based upon the technique of spectrographic analysis as described by C. C. Nitchie, "Quantitative Analysis with the Spectrograph," Industrial and Engineering Chemistry, Analytical Edition, Vol. 1, 1 (1929).

The medium standards shall be that which is nearest to the lead content of the sample as estimated from the preliminary plate (Section 4). Six recessed electrodes (Note 2) shall be treated (Section 3) with 0.1-ml. portions each of the standard solutions, preparing two electrodes for each of the three standards. Four electrodes shall be treated with 0.1 ml. each of the sample solutions, preparing two electrodes from the one sample solution and two from the duplicate sample solution. The electrodes shall be dried in an oven at 200°F. (93° C.) for about 30 min.

(*b*) Two spectral plates[71] shall be prepared each having five 2-min. exposures (Section 4 (*a*)) in the following order:

First spectral exposure	Low standard
Second spectral exposure	Sample
Third spectral exposure	Medium standard
Fourth spectral exposure	Sample
Fifth spectral exposure	High standard

The plate shall be adjusted for each exposure so that the spectral exposures are in juxtaposition, for ease of comparison with one another.

(*c*) From the finished plates, the lead content shall be estimated on the basis of a visual comparison of the difference in blackness between the lead lines in the spectrum of the sample and in the adjacent standard spectra. Two observers should independently evaluate the plates and the average of the estimations shall be considered as the lead content (Note 7) of the sample.

(*d*) If the iron and cadmium contents of the sample are within the limits set by the high and low standards used for the lead determination, the iron and cadmium may be determined with the same plates from which the lead was determined. If, however, this cannot be done, it will be necessary to repeat the spectrography[72] carried out for the lead determination using standards suitable for the iron and cadmium contents.

Testing for Compliance with Specifications

6. Frequently, the object of the spectrographic inspection is merely to determine whether the lead, iron and cadmium contents are less than certain amounts, as in the case of specification requirements on the composition. For this purpose the analytical procedure described in Sections 2 to 5 may be considerably simplified.

Procedure.—7. (*a*) *Standard Solution.*—One standard solution containing the maximum impurity contents allowed by the specifications shall be prepared to a concentration of 0.5 g. of metal per milliliter of hydrochloric acid solution.

(*b*) *Sample Solutions.*—Duplicate solutions of the sample shall be prepared as described in Section 2.

[71] The ten exposures may be recorded on one plate rather than two plates of five exposures each.

[72] It is not the intent of this method to limit to three the number of standards whose spectra are recorded on one plate. If it is necessary to use more than three standards for the analysis of one sample, the spectra of more than three may be photographed on one plate. The essential requirements are that the standard spectra be alternated with spectra of the sample and that at least two sample spectra be recorded from each sample solution.

(c) *Preparation of Electrodes.*—According to the method described in Section 3, the following electrodes shall be prepared: Four electrodes treated with the standard solution, two electrodes treated with the one sample solution and two electrodes treated with the duplicate sample solution.

(d) *Preparation of Spectra.*—Two spectral plates [73] shall be prepared each having four 2-min. exposures (Section 4 (a)) in the following order:

First spectral exposure	Standard solution
Second spectral exposure	Sample solution
Third spectral exposure	Sample solution
Fourth spectral exposure	Standard solution

(e) By visual comparison of the blackness of the lead, iron and cadmium lines (Note 6) of the standard spectra with the corresponding lines of the spectra of the samples, a determination may be made as to whether the composition of the sample is within the limits set by the specifications (Note 8).

Explanatory Notes

Note 1: *Acid and Distilled Water.*—The acid and distilled water shall be free from lead, iron and cadmium. The c.p. grade of acid may contain sufficient iron to introduce a significant error in the iron determination. In this event an iron-free acid of sufficient strength may be obtained by distilling the concentrated c.p. grade of hydrochloric acid, the distillate being absorbed in distilled water.

Note 2: *Electrodes.*—The electrodes shall be prepared from high-purity graphite rods, $\frac{5}{16}$-in. diameter being recommended (found by test to be free from iron, lead and cadmium). The electrodes which are to contain the sample shall be cut into 2-in. lengths and recessed at one end by drilling an axial hole about 0.15 in. in diameter and 0.25 in. in depth. Prior to use the electrodes shall be burned in a 10-amp. arc for about 2 min., by which treatment any impurities with which the electrodes may have been contaminated in the handling are volatilized.

Note 3: *Spectrography.*—The spectrograph shall have quartz optics or a diffraction grating of sufficient resolving power and dispersion to separate clearly the lines of the constituents to be determined from the lines of other elements present in the spectrum of the sample. In illuminating the slit of the spectrograph with the light from the arc, a quartz condensing lens (or lenses) shall be used in such a manner that the images of the electrode tips are sharply defined, one above, the other below, the open portion of the slit, in order to exclude the intense continuous spectrum of the hot carbon electrodes from the spectrograph. Adjustment of the distance between the electrodes shall be made, from time to time, in order to compensate for the burning away of the electrode tips. The same portion of the slit shall be used throughout, preferably the central portion. A moderately slow, fine-grained photographic plate is best suited for this method. Eastman 33 plate is an example of this type of plate. The following developer formula is suggested:

Stock Solution A:

Water	1000 ml.
Hydroquinone	42 g.
Anhydrous sodium sulfite	85 g.
Potassium bromide	3 g.
Citric acid	1.2 g.

Stock Solution B:

Water	1000 ml.
Anhydrous sodium carbonate	150 g.

For use take 100 ml. of Solution *A*, 80 ml. of Solution *B* and 420 ml. of water. Develop 4½ min. at 70° F. (21° C.). After development, the plate shall be washed, fixed and dried.

Note 4: *Standard Plate.*—A standard plate, on which are recorded the spectra of a series of standard solutions, shall be kept on hand for the purpose of the preliminary estimation (Section 4).

[73] The eight exposures may be recorded on one plate rather than on two plates of four exposures each.

NOTE 5: *Standard Solutions.*—Standard solutions shall be prepared as hydrochloric acid solutions of pure zinc with added lead, iron and cadmium in known ratio to the zinc. A uniform concentration of 0.50 g. of metal per milliliter shall be maintained. The standard solutions shall be prepared as follows:

Solution A (Zinc Stock Solution).—Pure zinc stock solution shall be prepared by dissolving in hydrochloric acid 100 g. of pure zinc, free from iron, lead and cadmium; the volume shall be adjusted to 200 ml.

Solution B (0.1 % Lead, 0.1% Iron, 0.1% Cadmium).—99.7 g. of pure zinc, 0.1 g. c.p. lead, 0.1 g. c.p. iron and 0.1 g. c.p. cadmium shall be dissolved in hydrochloric acid. The volume shall be adjusted to 200 ml. This is the starting or high standard solution corresponding to a zinc containing 0.1% each of lead, iron and cadmium. From this solution the next lower standard shall be made by dilution with pure zinc stock solution as follows:

Solution C (0.05% Lead, 0.05% Iron, 0.05% Cadmium).—To 10 ml. of Solution *B* shall be added 10 ml. of Solution *A*. This makes 20 ml. of a standard solution corresponding to a zinc containing 0.05% each of lead, iron and cadmium.

Solution D (0.025% Lead, 0.025% Iron, 0.025% Cadmium).—To 10 ml. of Solution *C* shall be added 10 ml. of Solution *A*. This makes 20 ml. of a standard solution corresponding to a zinc containing 0.025% each of lead, iron and cadmium.

Lower Standards.—The lower standards, 0.013, 0.0063, 0.0031, 0.0016, 0.0008, 0.0004, 0.0002, 0.0001, 0.00005%, shall be made similarly by the process of successive dilutions outlined for Solutions *C* and *D*. The larger volume of Solution *B*, which remains, may be stored in a sealed bottle for the replenishment of the supply of lower standards as required.

The limits of detection and quantitative estimation are approximately 0.0002% for lead, 0.0001% for iron and 0.00005% for cadmium. These limits are those experienced by one laboratory using a large Littrow type spectrograph. They are not invariable, however, and different laboratories will experience different values, depending upon experimental details.

NOTE 6: *Spectral Lines.*—The line used in grading the plate shall not be too dense or black since a very dense line does not show much change in appearance with change in concentration of the corresponding constituent element. The following table lists suitable lines for the estimation of lead, iron and cadmium in high-purity zinc together with an indicating of the approximate range of concentration in which the line is useful:

Elements to be Determined	Wave Lengths in International Angstroms of Suitable Lines	Range of Concentration in Which Line is Useful, Per Cent
Lead	2873.32 2663.17	0.1 to 0.01
	2833.07	0.1 to 0.0002
Iron	2845.59 2727.54 2714.42	0.1 to 0.05
	2625.68 3021.08 3020.50	0.05 to 0.0001
Cadmium	2980.62	0.1 to 0.05
	3261.05	0.05 to 0.001
	2288.03	0.002 to 0.00005

NOTE 7: *Precision.*—Experience has shown that the precision of determinations by this method is ±10 per cent of the amount of element being estimated.

NOTE 8: *Reliability of Test.*—Experiment has shown that this method of testing is capable of consistently detecting an off-grade composition if the concentration on lead, iron or cadmium is 20% or more higher than the corresponding concentration if the standard.

ZIRCONIUM AND HAFNIUM[1]

Zr, *at.wt.* 91.22; *sp.gr.* 6.4; *m.p.* about 1700° C.; *oxides*, ZrO_2, Zr_2O_5 and ZrO_3 in hydrated form)
Hf, *at.wt.* 178.6; *sp.gr.* probably between 12.1 and 13.3; *m.p.* about 2200° C.; *oxides*, only HfO_2 yet known with certainty

Since it has been recently shown that almost all zirconium compounds contain hafnium to the extent of 1 to 5% of the zirconium present, it must be borne in mind that, analytically speaking, what we term zirconium is really to be regarded as a mixture of zirconium and hafnium. As the percentage of hafnium is not determinable in practical analytical work, the results of analyses are simply reported as zirconium. It is evident that the only safe weighing form is zirconium dioxide, since analyses are commonly reported in percentages of ZrO_2, and any calculation involving a gravimetric factor is certain to be more or less inaccurate owing to the unknown value of the average atomic weight of the so-called zirconium in any particular case. Some of the fundamental data for zirconium have been corrected for hafnium content, but we must still regard the majority of these figures with less confidence in their exactness than in the case of most of the other elements.

The main ores of zirconium are baddeleyite, essentially zirconium dioxide; and zircon, essentially zirconium orthosilicate. While zircon is the most widely distributed ore, the most important commercially is now the Brazilian baddeleyite, which, mixed with a little zircon, comes under the trade name of zirkite, and contains around 75% of ZrO_2. Aside from the valuation of ores, the determination of zirconium is at times called for in furnace-lining material, high temperature laboratory ware, enamels, steel and other commercial products.

DETECTION

The material to be tested is brought into solution by one of the methods given in the section on the Preparation of the Sample. In the regular course of qualitative analysis the zirconium will be found in the main precipitate formed either by ammonium hydroxide alone or by the combined action of ammonium hydroxide and ammonium sulfide. This precipitate can be dis-

[1] Paul H. M.-P. Brinton, Consulting Chemist, Visiting Professor, University of Southern California, Los Angeles, Calif.

solved in sulfuric acid,[2] the acidity then adjusted so that 10% of the solution, by volume, is concentrated sulfuric acid, 10 ml. of 3% hydrogen peroxide and 1 ml. more of concentrated sulfuric acid added, and then a large excess of Na_2HPO_4 or $(NH_4)_2HPO_4$ solution, to which has also been added 1/10 of its volume of concentrated sulfuric acid. A white precipitate proves the presence of zirconium, since no other elements (titanium having been peroxidized) have phosphates which are insoluble in such an acid concentration.[3] This is the simplest and surest method of detecting zirconium. In the regular course of analysis thorium and the rare earths would probably have been precipitated from the acid solution of the ammonium hydroxide precipitate by an excess of oxalic acid (see "Detection" in chapter on thorium). The filtrate would contain almost all of the zirconium,[4] along with titanium, beryllium and the more common elements of the group. The oxalic acid in this filtrate can be destroyed by evaporation with sulfuric acid, and then zirconium, titanium and aluminum precipitated by boiling the weakly acid solution (containing 8 or 10 drops more sulfuric acid than is needed to redissolve the first faint precipitate formed by gradually adding dilute ammonia) with sodium thiosulfate. This precipitate may be brought into solution by fusing with potassium pyrosulfate, and taking up with sulfuric acid. The phosphate test as just outlined may then be applied.

Turmeric paper on drying after having been moistened with a slightly acid (HCl or H_2SO_4) solution containing zirconium shows a reddish-brown color, similar to that due to boric acid. Titanium gives a like reaction in the tetravalent condition, but if the acidified solution is reduced by adding a piece of zinc, and then promptly tested (before titanium is reoxidized), the test is specific for zirconium.

From aluminum zirconium may be differentiated by the solubility of zirconium basic carbonate in excess of a strong, cold solution of ammonium carbonate (on boiling the hydroxide separates out again); and by the insolubility of zirconium oxyiodate, produced by an alkali iodate in a slightly acid solution. (Thorium and tetravalent cerium also give the iodate test.)

[2] In presence of considerable phosphate much or all of the zirconium will be insoluble here, so any residue should be fused with sodium peroxide as described under Preparation and Solution of Sample. In the same way zirconium should be looked for in the insoluble residue left after the original decomposition of the sample, for it may be there either as phosphate, or as an hydrolysis product even in the absence of phosphoric acid.

[3] Biltz and Mechlenburg, Z. angew. Chem., 25, 2110, 1912; Lundell and Knowles, J. Am. Chem. Soc., 41, 1801, 1919.

[4] Oxalic acid produces a precipitation of zirconium oxalate in dilute mineral acid solution, but the precipitate is soluble in excess of oxalic acid. (It is also soluble in ammonium oxalate; and is not reprecipitated by addition of hydrochloric acid, thus differing from thorium.)

ESTIMATION

The readiness with which zirconium compounds undergo hydrolysis renders watchfulness necessary in cases where zirconium may be present. Thus small amounts of zirconium may be present in the insoluble residue or " silica " of an ordinary mineral analysis. It will remain after hydrofluoric acid treatment of the insoluble residue, and unless specifically determined it will be counted as aluminum. Also any zirconium in solution will be precipitated by ammonium hydroxide, and unless separated will be counted as aluminum if the latter is taken " by difference " from the analysis of the group precipitate.

PREPARATION AND SOLUTION OF THE SAMPLE

Acid treatment will not decompose ordinary zirconium ores. The following fluxes are most commonly used.

Sodium peroxide is used in a nickel crucible which has been lined by fusing some sodium carbonate,[5] and causing it to cool in an even layer on the sides and bottom. This prevents in large measure the attack of the crucible by the peroxide, and avoids the subsequent introduction of large amounts of nickel into the solution. Several grams of sodium peroxide are melted in the crucible, after lining with sodium carbonate, and allowed to solidify on the bottom. This prevents particles of the ore from being caught in the carbonate lining and remaining unfused. The sample of finely ground ore (0.5 g.) is mixed with 8–10 g. of sodium peroxide in the crucible thus prepared, and fused at low red heat over a small flame, by gently swirling the crucible, held in tongs. Five–ten minutes should suffice. When cool the crucible is placed in a large platinum dish, or porcelain casserole, and covered with warm water, keeping the vessel covered with a watch glass until danger of loss from effervescence is over, the solution is boiled until the carbonate lining has dissolved, and the crucible is then removed. The solution is next made decidedly acid with hydrochloric acid, and boiled until carbon dioxide is expelled. This should give a clear solution containing the zirconium and all the other constituents of the ore. If a very small amount of undecomposed ore is found here, it should be filtered off, ignited, fused with a little potassium pyrosulfate, dissolved in 5% sulfuric acid, filtered if necessary, and added to the main solution.

It has been recommended that fusion of zirconium ores with KOH which has first been melted down in the crucible and heated gradually to a temperature of 900° C., is preferable to fusion with sodium peroxide in a nickel crucible, sodium carbonate lined.

The sodium peroxide-charcoal method of Muehlberg [6] has been studied by Schumb and co-workers,[7] and it can well be used for the decomposition of zirconium ores. In a 50-ml. nickel crucible are placed about 25 g. of an intimate mixture (made by gently rolling the two constituents in a large dry bottle)

[5] Private communication from J. A. Holladay, Electro Metallurgical Co., Niagara Falls, N. Y.

[6] W. F. Muehlberg, J. Ind. Eng. Chem., 17, 690 (1925).

[7] G. G. Marvin with W. C. Schumb, J. Am. Chem. Soc., 52, 574 (1930); S. G. Simpson with W. C. Schumb, ibid., 53, 921 (1931).

of 15 parts of fine sodium peroxide with 1 part of 100-mesh pure sugar carbon. 1 g. of the finely ground sample is placed upon this mixture, covered with more fusion mixture and intimately mixed at the surface with a spatula. A liberal layer of the fusion mixture is used as a cover, and the crucible is immersed in cold, running water to a level slightly above that of the contents of the crucible. The ignition is started by means of the glowing tip of a cotton twine, and the crucible is immediately covered. After fusion is complete and the crucible is cold, the shrunken cake is placed in a 1-liter beaker and covered with 300 ml. of cold water. The crucible and cover are well rinsed off into the beaker. After heating nearly to boiling until the melt has disintegrated, the solution is diluted to about 900 ml. with hot water, and the heating is continued until the supernatant liquid is clear enough to filter. After filtration the residue is well washed with hot water, and the filtrate is discarded. (If the presence of much phosphate, or of even small amounts of tantalum or columbium is suspected, the residue is treated with hydrochloric acid and, without filtering, an excess of ammonia is added. The residue is filtered, ignited, and the fusion and leaching are repeated as above.) The residue is dissolved in hydrochloric acid, and any undissolved material is filtered off. This is essentially carbon, but it may contain a very small amount of undecomposed ore. If this is suspected the residue can be separately fused with sodium peroxide-carbon mixture, leached with water, dissolved in hydrochloric acid, and added to the main solution. To the hydrochloric acid solution 25 ml. of 18 N sulfuric acid are added, and evaporation is carried to heavy fumes. After cooling the mixture is diluted with water, and any silica is filtered off. The filtrate is made ammoniacal, the resulting precipitate is filtered, washed a few times with hot water, and dissolved in 15 ml. of 12 N hydrochloric acid. If the original ore contained only a low percentage of tantalum or columbium this solution is now ready for the determination of zirconium. If moderate or high percentages of tantalum or columbium were present the following modification should be adopted. The residue from the first peroxide-carbon fusion is treated with hydrochloric acid and, without filtering, excess of ammonium hydroxide is added. After filtration and partial washing with hot water, the residue is ignited and fused in a platinum crucible with about 20 times its weight of potassium carbonate. The fusion product is leached with hot water, filtered, washed with 2% potassium carbonate solution, and finally with hot water. If the percentage of columbium, and especially of tantalum, is quite high, the fusion with potassium carbonate and the leaching should be repeated. The residue is finally ignited, and fused in the original platinum crucible with potassium pyrosulfate. The fused mass is extracted with 200 ml. of hot water containing 10 ml. of 18 N sulfuric acid. After precipitation by ammonium hydroxide, filtration, and washing with hot water, the precipitate is dissolved in 15 ml. of 12 N hydrochloric acid, and the solution is now ready for the determination of zirconium.

Potassium hydrogen fluoride is applied by Smith and James [8] in the following manner: The finely ground ore is fused with 12 to 15 times its weight of potassium hydrogen fluoride. The latter may be prepared from potassium carbonate or fluoride by treating with a slight excess of hydrofluoric acid, and evaporating over a small flame until a clear fused mass is obtained. When cool the melt may be broken up and preserved for use. The mixture of ore

[8] Smith and James, J. Am. Chem. Soc., 42, 1764 (1920).

and fluoride, in a platinum dish, is carefully heated over a small flame. When the mixture has softened it is stirred with a platinum rod, and the size of the flame is gradually increased, finally heating over a Meker burner until the mass just fuses to a clear liquid.[9] The cooled melt is treated with 50 ml. of 1 : 1 sulfuric acid, gently heated until nearly all water is expelled, and then more strongly until abundant fumes are evolved. The cold residue is boiled with water. This solution contains all the zirconium. If it is to be used for the selenite method of Smith and James, the zirconium is precipitated (along with many other bases) by ammonium hydroxide, filtered, washed free from sulfates—since sulfates are undesirable for the selenious acid precipitation—and dissolved in hydrochloric acid.

Borax is strongly recommended by Lundell and Knowles[10] for the decomposition of all ores of zirconium. This flux is particularly suited to the decomposition of samples in which zirconium only is to be determined, and by precipitation with cupferron, since boric acid does not interfere with this reagent. If other elements of the sample are to be determined, the boric acid must be removed by volatilization as methyl borate, so in such cases it is better to employ the sodium peroxide fusion. In using the borax method Lundell and Knowles recommend the following procedure: 4 g. of the flux are melted in a platinum crucible and allowed to cool. About 0.3 g. of the finely ground ore is placed on top of the fused borax, the crucible is covered, and heated over a Meker burner until thorough fusion has taken place, which does not ordinarily require more than half an hour. During the operation it is well to stir the melt occasionally with a short platinum rod or stiff wire, which is allowed to remain in the crucible, and which may be conveniently handled with the crucible tongs. When the decomposition of the ore is complete, the platinum rod is removed, and it is put into the beaker to be used for the solution of the melt. As the melt cools, the crucible is gently twirled in order to run the fusion up on the sides in a thin layer. The cooled melt is dissolved in 150 ml. of 1 : 5 hydrochloric acid in a 250-ml. beaker, by filling the crucible with acid, inverting in such a manner that one edge of the crucible rests on the crucible cover, which has been placed on the bottom of the beaker—thus allowing free circulation of the solvent—and then gently warming on the steam bath. The solution is transferred to a platinum dish or porcelain casserole, 20 ml. of 1 : 1 sulfuric acid are added, and the mixture is evaporated until heavy fumes escape.[11] The cooled solution is next diluted to about 100 ml., the impure silica is filtered off and washed with hot water. This solution is allowed to stand warm over night. If the ore contained interfering amounts of phosphorus, it will be thrown down as zirconium phosphate by this digestion. If a precipitate appears, it is filtered and washed with 5% ammonium nitrate solution. This precipitate will contain zirconium, and

[9] Experiments in the writer's (Brinton's) laboratory by Dr. Tohru Kameda indicate that there is no loss of zirconium by volatilization if the process is carried out as here described. Continuing the heating for 5 minutes after clear fusion has been attained may cause a loss of as much as 2 mg. of ZrO_2.

[10] Lundell and Knowles, J. Am. Chem. Soc., 42, 1439 (1920).

[11] During the evaporation boric acid will separate and form a crystal skin over the surface, thus retarding evaporation. Occasional stirring during this period will hasten the evaporation. As the sulfuric acid becomes more concentrated by evaporation, the boric acid eventually dissolves again.

there is still apt to be a little zirconium in the impure silica first filtered off. Also there may be some phosphoric acid in the filtrate; so to this filtrate 5 g. of ammonium chloride, and then ammonium hydroxide in slight excess are added, and after boiling for several minutes, the precipitated hydroxides are filtered and washed with 2% ammonium nitrate solution. This filtrate is discarded. The precipitate and paper are digested in 100 ml. of hot 5% sulfuric acid solution, and the filter shreds and any insoluble residue are filtered and well washed with hot water. This solution, containing most of the zirconium of the sample, is temporarily set aside. The last residue filtered, the impure silica, and any zirconium phosphate obtained by the over-night digestion are all ignited in the original platinum crucible. The ignition residue is moistened with water, 1 ml. of 1 : 1 sulfuric acid, and 5 ml. of hydrofluoric acid are added, and the mixture is heated until all sulfuric acid has been expelled. The residue in the crucible is fused with a little sodium carbonate, digested in water, and filtered, washing with hot water. The filtrate is discarded. The insoluble residue is again ignited in the platinum crucible, fused with potassium pyrosulfate; and, after cooling, the melt is dissolved in hot 5% sulfuric acid. This solution is added to the main solution, thus giving one solution in which is contained all the zirconium originally present in the sample.

SEPARATIONS

From Members of the Copper and Tin Groups.—The members of these groups are precipitated free from zirconium by hydrogen sulfide in slightly acid solution.

From Iron, Nickel, Cobalt, Manganese, and Zinc.—The iron, in acid solution, is reduced by hydrogen sulfide gas, tartaric acid equal to 5 times the approximate weight of the oxides present is added, the solution is made ammoniacal, and then hydrogen sulfide is passed into the solution until the sulfide precipitate has coagulated. The precipitate is filtered on close-grained paper, care being taken to keep the funnel well filled, so that oxidation of the sulfides and consequent "running through" is avoided. The sulfides are promptly washed, using the same precaution, with water containing a little ammonium chloride and ammonium sulfide. If the cupferron precipitation of zirconium is to be used, the tartrate need not be destroyed, and it is sufficient to acidify to a total acidity of 10% of concentrated sulfuric acid (by volume), and to boil out the hydrogen sulfide. If for further work it should be necessary to remove the tartrate, the solution is acidified with 10 ml. of concentrated sulfuric acid, evaporated to a volume of about 50 ml., 10 ml. of concentrated nitric acid added, and the solution evaporated to fumes of sulfur trioxide. After cooling, 10 ml. of concentrated nitric acid are again added, and the

mixture once more evaporated to fumes. At times a third addition of nitric acid and evaporation may be necessary to completely destroy the tartaric acid.

From Titanium.—Zirconium may be separated from titanium by precipitating the zirconium with Na_2HPO_4 or $(NH_4)_2HPO_4$ in a 10% (by volume) sulfuric acid solution, in presence of hydrogen peroxide. See Gravimetric Determination as phosphate.

Powell and Schoeller[12] recommend the separation of zirconium from titanium by precipitation of the latter by tannin from a neutralized oxalate solution which is half saturated with ammonium chloride.

From Thorium and Rare Earth Elements.—These elements may be precipitated with an excess of oxalic acid, leaving the zirconium in the filtrate. (See "Detection" in chapter on Thorium.) For complete separation the rare earth oxalates should be boiled with concentrated sulfuric acid until decomposed, diluted, nearly neutralized with ammonia, and again precipitated with an excess of oxalic acid. The combined filtrates contain all the zirconium. (A method adapted to the determination of small amounts of rare earth oxides in the cupferron precipitate is given later.)

From Aluminum, Chromium, and Uranium.—Zirconium is quantitatively separated from these three elements by precipitation with cupferron in 10% (by volume) sulfuric acid solution. The uranium must be in the hexavalent condition or it will contaminate the zirconium precipitate. (Nitric acid should not be used to oxidize uranium, as it decomposes cupferron. Uranium will practically always be in the hexavalent condition without special oxidation. If in doubt, the 10% sulfuric acid solution may be boiled with a little hydrogen peroxide.)

From Molybdenum.—By precipitation of molybdenum sulfide in acid solution. (See chapter on Molybdenum.)

From Tungsten.—By precipitation of tungsten in acid solution by cinchonine hydrochloride. (See chapter on Tungsten.)

From Vanadium.—By fusion of the mixed oxides with sodium peroxide or sodium carbonate, and leaching out the soluble sodium vanadate with water.

GRAVIMETRIC DETERMINATION OF ZIRCONIUM

By Precipitation with Cupferron.—Precipitation of zirconium, etc., with cupferron in a cold 10% H_2SO_4 solution containing alkali salts (sodium and potassium), filtering and washing and igniting to ZrO_2, causes high results. It is essential that the alkali salts be first removed by precipitation with ammonia and filtration and the precipitate dissolved in 10% sulfuric acid.

[12] A. R. Powell and W. R. Schoeller, Analyst, 55, 605, 1930; ibid., 57, 550, 1932. The procedure is given in detail in Chemical Abstracts, 25, 51 (1931).

The solution, which has a volume of 300–400 ml., and contains 10% (by volume) of concentrated sulfuric acid (any tartaric acid present does not interfere), is cooled to about 10° C., and then an excess of cupferron solution (6 g. dissolved in 100 ml. of cold water and filtered) is added. The formation of a fine white precipitate (nitrosophenylhydroxylamine) which redissolves shows that an excess of the reagent has been added. The zirconium precipitate is white and curdy, but any titanium present is also quantitatively precipitated, and it will impart a yellow color to the precipitate. A brownish color indicates that the previous separation from iron has been faulty. The precipitate is filtered and washed with cold 1 : 10 hydrochloric acid solution. The precipitate and paper are carefully ignited in a weighed platinum crucible, very slowly until the rush of gases from decomposition of the organic matter has ceased; and then to constant weight over a blast or over a large Meker burner. The weight thus found represents all the zirconium and titanium dioxides, and some rare earth oxides, if these elements have not previously been completely removed.

To correct for titanium and rare earths the ignited oxides are fused with potassium pyrosulfate, dissolved in 1 : 10 sulfuric acid, and diluted to exactly 100 ml. in a graduated flask. By means of a *dry* 50–ml. pipette exactly one-half of the solution is taken for the determination of titanium, and the pipette and the 100–ml. flask are completely rinsed into another vessel, thus giving the other half for the determination of rare earths.

Small amounts of titanium are determined by the colorimetric method; while for larger amounts the zinc reductor—permanganate titration method —is used. For details of these see chapter on Titanium.

Rare earths may be determined according to Hillebrand's method [13] as follows: " Precipitate the hydroxides with an excess of potassium hydroxide, decant the liquid, wash by decantation with water once or twice and then slightly on the filter. Wash the precipitate from the paper into a small platinum dish, treat with hydrofluoric acid, and evaporate nearly to dryness. Take up in 5 ml. of 5% (by volume) hydrofluoric acid. If no precipitate is visible, rare earths are absent. If a precipitate is present, collect it on a small filter held by a perforated platinum or rubber cone and wash it with from 5 to 10 ml. of the same acid. Wash the crude rare earth fluorides into a small platinum dish, burn the paper in platinum, add the ash to the fluorides and evaporate to dryness with a little sulfuric acid. Dissolve the sulfates in dilute hydrochloric acid, precipitate the rare earths by ammonia, filter, redissolve in hydrochloric acid, evaporate the solution to dryness, and treat the residue with 5 ml. of boiling hot 5% oxalic acid. Filter after fifteen minutes, collect the oxalates on a small filter, wash with not more than 20 ml. of cold 5% oxalic acid, ignite and weigh as rare earth oxides which are to be deducted from the weight of the cupferron precipitate."

While the recovery of the rare earths by this method is not absolutely complete, the error is negligible for the amounts ordinarily found.

The sum of the weights of rare earth oxides and titanium dioxide found are subtracted from the weight of the ignited cupferron precipitate to obtain the true weight of ZrO_2.

[13] W. F. Hillebrand, The Analysis of Silicate and Carbonate Rocks, U. S. Geol. Survey Bulletin 700, p. 176; Lundell and Knowles, loc. cit., p. 1446.

By Precipitation with Selenious Acid.[14]—To the nearly neutral solution, which should be free from phosphate, sulfate, columbium and tantalum, and which should have a volume not much greater than 100 ml., 20 ml. of 12 N hydrochloric acid and 20 ml. of alcohol are added. The solution is heated nearly to boiling, diluted to 500 ml., again heated to boiling, and 20 ml. of 10% selenious acid solution are added. After standing hot until the supernatant liquid is sufficiently clear for filtration (preferably not over 2 hours), the precipitate is filtered and washed a few times with hot water. The paper is punctured and the precipitate is washed into the original beaker with as little hot water as possible. The paper is set aside for further treatment. 15 ml. of 12 N hydrochloric acid are added to the contents of the beaker and the mixture is heated until the precipitate is dissolved. (A slight turbidity may be neglected.) Twenty ml. of 3% hydrogen peroxide are added, the solution is warmed, diluted to 500 ml., heated to boiling and again precipitated with 20 ml. of 10% selenious acid solution. After filtration, and washing with hot water, the paper is again punctured, and the precipitate is rinsed into the original beaker.

(*A*) In a small beaker the two papers are digested with 40 ml. of hot 10% oxalic acid solution. The pulp is filtered and washed, and the filtrate and washings are added to the zirconium precipitate. The mixture is diluted to 200 ml., heated to boiling, and 12 ml. of 6 N hydrochloric acid are added. After allowing to stand at room temperature for at least 10 hours, the precipitate is filtered and washed with a solution containing 40 ml. of 6 N hydrochloric acid and 25 g. of oxalic acid per liter. To the filtrate 30 ml. of 18 N sulfuric acid are added, and evaporation on the water-bath is started. (If the oxalate precipitate is large it is flushed off into a 400 ml. beaker, 5 ml. of 18 N sulfuric acid are added, and the mixture is evaporated on the water-bath until oxalate has been destroyed, as shown by the cessation of gas bubbles. The solution is diluted with water, made ammoniacal, and the precipitate is filtered, and dissolved in 12 ml. of 6 N hydrochloric acid. After diluting to 160 ml., and heating to boiling, 40 ml. of 10% oxalic acid solution are added. After standing for at least 10 hours the solution is filtered into the main solution. The solution is now evaporated on the water-bath until oxalate is destroyed, the sides of the beaker and the watch glass are rinsed down, and any precipitated selenium is filtered off. If a small amount of red selenium runs through the paper it may be neglected. The solution is made ammoniacal, and the precipitate is filtered and washed a few times with hot water. The paper is punctured, and the precipitate is flushed off with as little hot water as possible. Fifteen ml. of hot 12 N hydrochloric acid are poured over the paper into the zirconium hydroxide suspension, and the mixture is heated until the precipitate is entirely dissolved.

(*B*) Twenty ml. of 3% hydrogen peroxide are added, and the solution is warmed, diluted to 500 ml., and heated to boiling. Twenty ml. of 10% selenious acid solution are added, and the precipitate is filtered after the supernatant liquid is clear. After ignition over the Bunsen flame, and finally for 5 minutes over the Méker burner the ZrO_2 is weighed.

In the known absence of thorium the above method may be shortened by omitting the oxalate precipitation involved in the above directions from (*A*)

[14] The method of Smith and James, J. Am. Chem. Soc., 42, 1764 (1920), modified by Simpson and Schumb, ibid., 53, 921 (1931).

to (*B*). In this case, the zirconium selenite precipitate obtained at (*A*) is dissolved by adding 20 ml. of 12 N hydrochloric acid, and heating to boiling. The method is continued from the point (*B*). The two filter papers from which the first two precipitates were washed are ignited, and the weight of their ignition products are added to the final weight of ZrO_2.

By Precipitation with Ammonium Phosphate.—This method is suitable for separations, and for the determination of small amounts of zirconium such as are encountered in rock analysis. In view of the probability that almost all minerals of zirconium contain appreciable amounts of celtium hafnium, which gives practically all the reactions of zirconium, but which has a very much higher atomic weight, an uncertainty as to the factor ZrO_2/ZrP_2O_7 exists, so the pyrophosphate can hardly be recommended as a weighing form for large amounts of zirconium. The following details are recommended for observance in using this method.[15]

A. Volume of Solution.—From 25 ml. for small amounts (i. e. 0.0005g. ZrO_2) to 200 ml. for amounts ranging around 0.1 g ZrO_2.

B. Acidity.—Twenty per cent sulfuric acid by weight.

C. Hydrogen Peroxide.—Sufficient to keep titanium peroxidized; 10 ml. will do no harm.

D. Precipitant.—Secondary ammonium phosphate in excess. From 10 to 100 times the theoretical requirement, as expressed by the ratio Zr : P_2O_5, should be used here. The large excess is desirable when small amounts of zirconium are determined.

E. Precipitation Conditions.—(1) Temperature: Cold or tepid, preferably 40–50° C. (2) Time: Two hours for amounts of ZrO_2 in excess of 0.005 g. Six hours, or longer, for smaller amounts.

F. Filtration.—Warm solution, decant as far as possible to avoid clogging the filter.

G. Washing.—This should be done with cold 5% ammonium nitrate, since the phosphate is appreciably soluble in pure water.

H. Ignition.—Ignite very carefully in a partially covered platinum crucible over a low flame until carbon is destroyed, then blast or heat over a Méker burner for 15 minutes.

By Precipitation with Phenylarsonic Acid.[16]—This precipitation method serves to separate zirconium from most other elements. The zirconium and other bases should be in about 10% (by volume) hydrochloric acid solution, though solutions containing up to about 50% of their volume of concentrated hydrochloric acid are said to exert no inappreciable solvent action on zirconium phenylarsonate. An excess of a 10% solution of phenylarsonic acid[17] is added and the mixture is heated to boiling, being well stirred in the meantime, filtered, and washed with 1% hydrochloric acid solution. A single precipitation is sufficient to separate zirconium from the majority of elements, even from the rare-earths. From iron the separation is incomplete after one precipitation,

[15] Lundell and Knowles, J. Am. Chem. Soc., 41, 1806 (1919); Hillebrand, op. cit., p. 173; Nicolardot and Reglade, Compt. rend., 168, 349 (1919).

[16] Rice, Fogg and James, J. Am. Chem. Soc., 48, 895 (1926). See also P. Klinger, Tech. Mit. Krupp, 3, 1 (1935).

[17] The reagent may be conveniently prepared by the method of Palmer and Adams, J. Am. Chem. Soc., 44, 1361 (1922).

but if the amount of iron originally present does not greatly exceed that of the zirconium, the iron may be removed by digesting the first precipitate and paper with 1 : 1 hydrochloric acid until well disintegrated, diluting then to about 500 ml. and adding 15 ml. more of the phenylarsonic acid reagent. If the amount of iron originally present is very large the first precipitate and paper should be warmed with 15 ml. of 1 : 1 sulfuric acid until the precipitate has dissolved, after which 50 ml. of concentrated hydrochloric acid are added, the solution diluted to about 500 ml., boiled and treated with 30 ml. of the phenylarsonic acid solution. This precipitate is free from iron. In the presence of thorium or uranium reprecipitation from sulfuric acid solution, as in the case of large amounts of iron, is necessary. The separation from titanium is complete in one precipitation, if carried out in about 500 ml. of 10% hydrochloric acid solution to which has been added 35 ml. of 3% hydrogen peroxide, using in this case a liberal excess (about 35 ml.) of phenylarsonic acid.

Simple ignition of the zirconium phenylarsonate gives results which are a little high, due to retention of arsenic, but if the ignition is finished over the blast in a current of hydrogen the results are correct.

RECOMMENDED METHOD FOR THE DETERMINATION OF ZIRCONIUM IN COMMERCIAL ZIRCONIUM ORES

The following combination gives a method essentially as recommended by the U. S. Bureau of Standards. Details will be found in the respective sections of this chapter.

Decomposition by fusion of 0.3 g. sample with borax, following the procedure under " Preparation and Solution of the Sample " until the sulfuric acid solution containing all the zirconium originally present in the sample is obtained.

Separation from members of the copper and tin groups by precipitation with hydrogen sulfide in an approximately 1% sulfuric acid solution; and then, without intervening filtration, separation from iron, manganese, etc., by treatment with tartaric acid, ammonia, and hydrogen sulfide, as detailed under " Separations," finally obtaining the zirconium in 10% (by volume) sulfuric acid solution. (Removal of tartaric acid is not necessary.)

Precipitation with cupferron, with subsequent corrections for any titanium and rare earths present, just as outlined in the " Gravimetric Determination."

DETERMINATION AS ZIRCONIUM OXIDE

With pure salts the zirconium may be precipitated completely as the hydroxide by the addition of ammonia, settling and finally igniting and weighing as the oxide, ZrO_2.

The Separation of Zirconium from Hafnium.—No single precipitation method suitable for the separation of zirconium from hafnium has yet been found, and all processes involve tedious fractionation. Current patent literature is rich in proposed methods, but the most reliable is the fractional crystallization of the double potassium or ammonium fluorides.[18] Fractional precipitation of the phosphates [19] leads as quickly to the separation, but the gelatinous precipitates are somewhat inconvenient to handle. Prandtl [20] suggests the fractional precipitation of the ferrocyanides.

A rough estimate of the percentage of HfO_2 in a mixture of the dioxides of zirconium and hafnium may be obtained from a determination of the density. The density of HfO_2 is 9.67 and that of ZrO_2 is 5.73. From the observed density, D, of the mixture the percentage of HfO_2 is calculated as follows:

$$\%\ HfO_2 = \frac{D - 5.73}{3.94} \times 100.$$

Chemically the percentage of HfO_2 in a mixture with ZrO_2 can be estimated by conversion to bromides, or to the anhydrous sulfates, and from the differences in weight between the compounds the percentages of each constituent can be calculated by conventional methods for indirect analysis.[21]

Zirconium in Plain Carbon and Alloy Steels.—See Vol. II under Steel Analysis.

[18] von Hevesy and Jantzen, Chem. News, **127**, 353 (1923).
[19] von Hevesy and Kimura, J. Am. Chem. Soc., **47**, 2542 (1925); de Boer and van Arkel, Z. anorg. allgem. Chem., **148**, 86 (1925).
[20] W. Prandtl, Z. anorg. allgem. Chem., **208**, 420 (1932).
[21] G. von Hevesy, Das Element Hafnium (book) (1927), page 34.

VOL. I

PART II

QUALITATIVE TESTS OF SUBSTANCES

QUALITATIVE TESTS OF SUBSTANCES

BLOWPIPE AND FLAME TESTS OF SOLIDS

BLOWPIPE TESTS ON CHARCOAL

Heat a small portion of the material on charcoal in the reducing flame, using a blowpipe. Scoop out a round hole in the charcoal, place a little of the substance in the cavity, and direct the inner flame of the blowpipe against it at an angle of thirty degrees.

Result of Test	Inference
Melts and runs into the charcoal	Alkalies, K, Na, etc.
An alkaline residue on charcoal	Ca, Sr, Ba, Mg
A residue which, when moistened with a drop of $Co(NO_3)_2$ and heated in O. F., produces a color which is blue	Aluminum, silicon
Produces a color which is green	Zinc, tin, antimony
Produces a color which is red	Barium
Produces a color which is pink or rose-red	Manganese
Deflagrates	Nitrates, chlorates
Leaves an incrustation which is white near the flame	Antimony
White, garlic odor	Arsenic
Dark red	Silver
Red to orange	Cadmium
Lemon yellow (hot), light yellow (cold)	Lead
Orange yellow (hot), light yellow (cold)	Bismuth
Yellow (hot), white (cold)	Zinc or tin, latter nonvolatile

Blowpipe Tests.—Substance fused with Na_2CO_3 on charcoal. Place a small amount of the substance on charcoal with a little sodium carbonate, and fuse, using reducing flame.

Result of Test	Inference
Metallic globules, without incrustation	
Yellow flakes	Gold
Red flakes	Copper
White globule, moderately soft	Silver
Metallic globules, with incrustation	
White, moderately soft beads	Lead or tin (volatilized lead leaves yellow coat)
White, brittle beads	Bismuth or antimony (yellowish)
Yellow in O. F.	Chromium
Green in O. F.	Manganese
A substance (in R. F.) which, when moistened and placed on a silver coin, leaves a brown or black stain	Sulfur compounds

Test	Inference
Dark gray magnetic powder which, when moistened on a filter paper with a drop of dilute HCl and HNO_3, and gently dried over a flame, leaves a stain which is faint pink, turning blue	Cobalt
Green stain, turning yellow	Nickel
A stain turned blue by $K_4Fe(CN)_6$	Iron

In place of using charcoal the above tests may be made with a splinter of wood covered with a coating of fused Na_2CO_3. The test is made by dipping the heated splinter into a mixture of the powdered substance with fused sodium carbonate and plunging for a moment in the reducing flame. Examine the material on the splinter, scrape off on a piece of glazed paper and examine.

Blowpipe Test.—Substance moistened with cobalt nitrate solution and ignited.

Color of Residue or Incrustation	Inference
Brick red	BaO
Pink	MgO
Gray	SrO, CaO
Yellowish green	ZnO
Dark muddy green	Sb_2O_5
Bluish green	SnO
Blue	Al_2O_3, SiO_2

FLAME TEST

Flame Test. Moisten a platinum wire in concentrated HCl, dip into the powdered substance and insert into a Bunsen flame. If sodium is prominent, examine through a blue glass. (Test the cobalt glass to see if it is effective in cutting out the yellow sodium light by examining a sodium flame through it.)

Flame Color	Color through Blue Glass	Element
Carmine red	Purple	Lithium
Dull red	Olive green	Calcium
Crimson	Purple	Strontium
Golden yellow	Absorbed	Sodium
Greenish yellow	Bluish green	Barium, molybdenum
Green		Cu, $-PO_4$, $-B_2O_3$,
Blue		Cu, Bi, Pb, Cd, Zn, Sb, As
Violet	Violet red	Potassium

The platinum wire should be cleaned before making the test. This can be accomplished by dipping it into concentrated HCl and holding it in the Bunsen, or, better, a flame of a blast lamp, until the flame is no longer colored. Repeatedly dipping into the HCl may be necessary.

Examine the flame through a spectroscope, if available, and compare the spectra with a spectra chart. Mere traces of the alkali and alkaline earth metals can be detected in this way by their characteristic spectral lines.

Behavior of Substances fused with Microcosmic Salt and Borax Beads

A clear bead is formed by fusing the flux on a loop of platinum wire. Dip the bead in the finely powdered substance to be examined, and heat again—first in the oxidizing flame; second in the reducing or inner flame. Metallic salts are mostly changed to oxides. **In the Table**—*h.* signifies hot; *c.*, cold; *sups.*, supersaturated with oxide; *s. s.*, strongly saturated; *h. c.*, hot and cold.

Color of the Bead.	With Microcosmic Salt, Sodium Ammonium Hydrogen Phosphate.		With Sodium Tetraborate (Borax).	
	In outer or oxidizing Flame.	*In inner or reducing Flame.*	*In outer or oxidizing Flame.*	*In inner or reducing Flame.*
Colorless.	**Si** (swims undissolved). **Al, Mg, Ca, Sr, Ba, Sn** (*s. s., opaque*). **Ti, Zn, Cd, Pb, Bi, Sb** (*not sat.*).	**Si** (swims undissolved). **Al, Mg, Ca, Sr, Ba** (*sups. not clear*). **Ce, Mn, Sn.**	*h. c.*: **Si, Al, Sn** (*sups. opaque*). **Al, Mg, Sr, Ca, Ba, Ag** (*not sat.*). **Zn, Cd, Pb, Bi, Sb, Ti, Mo.**	**Si, Al, Sn** (*s. s. opaque*). Alkaline earths and earths. *h. c.*: **Mn, Ce.** *h.*: **Cu.**
Yellow or Brownish.	*h.* (*s. s.*): **Fe, U, Ce.** *c.*: **Ni.**	*h.*: **Fe, Ti.** *c.*: **Ni.**	*h., not sat.*: **Fe, U.** *h., sups.*: **Pb, Bi, Sb.**	*h.*: **Ti, Mo.**
Red.	*h.* (*s. s.*): **Fe, Ni, Cr, Ce.**	*c.*: **Cu.** *h.*: **Ni, Ti with Fe.**	*h.*: **Fe, Ce.** *c.*: **Ni.**	*c.*: **Cu** (*sups. opaque*).
Violet or Amethyst.	*h. c.*: **Mn.**	*c.*: **Ti.**	*h. c.*: **Mn.** *h.*: **Ni with Co.**	*c.*: **Ti.**
Blue.	*h. c.*: **Co.** *c.*: **Cu.**	*h. c.*: **Co.** *c.*: **W.**	*h. c.*: **Co.** *c.*: **Cu.**	*h. c.*: **Co.**
Green.	*h.*: **Cu, Mo; Fe with Co or Cu.** *c.*: **Cr.**	*c.*: **Cr.** *h.*: **U, Mo.**	*c.*: **Cr.** *h.*: **Cu, Fe with Co.**	**Cr.** *sups.*: **Fe.**
Gray and Opaque.		**Ag, Pb, Sb, Cd, Bi, Zn, Ni.**		**The same as with microcosmic salt.**

TABLE FOR REVIEW OF THE SEPARATI

Solvents in order of preference—H_2O, dil. HCl, conc. HCl, dil. HNO_3, conc. HNO_3, aq. reg. Refractory Substances—H_2SO_4+HF, fusions with Na_2CO_3, $KHSO_4$, NaOH or KOH. Analysis— Neutral or slightly acid solutions of the salts of —

Pb, Hg′, Ag, As‴, As^V, Sb^V, Sb‴, Sn^{IV}, Sn″, Au‴, Pt^{IV}, Mo^{VI}, Hg″, Pb, Bi, Cu′, Cu″, Cd, Al, Cr‴, Cr^{VI}, Fe″, Fe‴, Co, Ni, Mn″, Mn^{VII}, Zn, Ba, Sr, Ca, Mg, K, Na, NH_4

Add hydrochloric acid.

Precipitate. (1) Silver Group.

$PbCl_2$ (w)	Add hot water.	Sol. $PbCl_2$	Tests (a) $+H_2SO_4 = PbSO_4$ white. (b) $+H_2S = PbS$ b	
HgCl (w)		Res. HgCl	Add NH_4OH	Residue—NH_2HgCl+Hg black.
AgCl (w)		AgCl		Solution—$(NH_3)_2(AgCl)$ } acidify w

Solution. Pass hydrogen sulfide gas into the warm solution.

(2) Tin and Copper Group. Precipitate. Add yellow ammonium sulfide.

Precipitate	Solution.	Add dilute hydrochloric acid. Precipitation of Tin Group.	Dissolve in HCl with the aid of $KClO_3$.
As_2S_3 (y)	$(NH_4)_3AsS_4$	As_2S_5	H_3AsO_4
As_2S_5 (y)	$(NH_4)_3AsS_4$	As_2S_5	......
Sb_2S_5 (o)	$(NH_4)_3SbS_4$	Sb_2S_5	$SbCl_5$
Sb_2S_3 (o)	......	......	......
SnS_2 (y)	$(NH_4)_2SnS_3$	SnS_2	$SnCl_4$
SnS (br)	......	......	......
Au_2S_3 (br)	Solution.	Au_2S_3	$AuCl_3$
PtS_2 (bk)	Solution.	PtS_2	$PtCl_4$
MoS_3 (br)	$(NH_4)_2MoS_4$	MoS_3	$MoCl_6$

Copper Group.

Precipitate	Residue.	Digest in hot dilute HNO_3.	Add 2 or 3 drops of dilute H_2SO_4.
HgS (bk)	HgS	HgS	Dissolve in nitrohydrochl
PbS (bk)	PbS	$Pb(NO_3)_2$	Ppt. $PbSO_4$ (
Bi_2S_3 (br)	Bi_2S_3	$Bi(NO_3)_3$	Solution. $Bi(NO_3)_3$
Cu_2S (bk)	Cu_2S	$Cu(NO_3)_2$	$Cu(NO_3)_2$
CuS (bk)	CuS	.....	.....
CdS (y)	CdS	$Cd(NO_3)_2$	$Cd(NO_3)_2$

Solution. Cr^{VI} becomes Cr‴, Fe‴ becomes Fe″ and Mn^{VII} becomes Mn″. Boil to expel H_2S, add HNO_3 and boil to oxidize ferrosum; and add ammonium chloride and ammonium hydroxide.

(3) Iron Group. Precipitate. Boil with NaOH.

Precipitate		
$Al(OH)_3$ (w)	Sol. $NaAlO_2$	Add NH_4Cl or render a
$Cr(OH)_3$ (g)	Res. $Cr(OH)_3$	Fuse on platinum. KNO_3 and Na_2CO_3. Extract with wate
$Fe(OH)_3$ (r)	$Fe(OH)_3$	

Solution. $MnCl_2.2NH_4Cl$, $(NH_4)_2ZnO_2$, and $MgCl_2.NH_4Cl$ are formed; also soluble double compounds of Co and Ni with ammonium hydroxide.

Add hydrogen sulfide to the strongly ammoniacal solutions.

(4) Zinc Group. Precipitate. Digest with cold dilute HCl.

Precipitate	
CoS (bk)	Res. CoS
NiS (bk)	NiS
MnS (pk)	Sol. $MnCl_2$
ZnS (w)	$ZnCl_2$

Solution. Add NH_4OH and $(NH_4)_2CO_3$.

(5) Calcium Group. Precipitate. Dissolve in $HC_2H_3O_2$

Precipitate
$BaCO_3$
$SrCO_3$
$CaCO_3$

Solution. Add Na_2HPO_4 to a portion, and if a precipitate is obtained, use $(NH_4)_2HPO_4$ with the other portion and filter.

Abbreviations: (w) = white; (y) = yellow; (o) = orange; (br) = brown; (bk) = bl

F THE METALS. ANALYSIS OF THE SOLUTION.

) $+K_2CrO_4 = PbCrO_4$ yellow. (*d*) $+KI = PbI_2$ yellow.

$)_2 = AgCl$ white.

AsH_3 gas ...... | Conduct the gas into $AgNO_3$ sol. Also obtain mirror and spots. | H_3AsO_3 } Remove $AgNO_3$ with $CaCl_2$ and add H_2S { As_2S_3 Lemon yellow. Gützeit Test—AsH_3 colors $HgCl_2$ paper a deep maroon.

SbH_3 gas + Sb ...... | $SbAg_3$ } Dissolve in hot HCl, dilute, filter and add H_2S { Sb_2S_3 Orange.

Sn .. Au Pt | Digest with warm HCl. | $SnCl_2$ } Test with $HgCl_2$. { $HgCl$ White; or Hg Gray.

Sb, Au, Pt | Dissolve in nitrohydrochloric acid | $SbCl_5$, $AuCl_3$, $PtCl_4$ | Boil with solution $FeSO_4$ | $SbCl_5$ reject or test in Marsh apparatus.

Au, Pt } Dissolve in nitrohydrochloric acid, evaporate to dryness with excess of NH_4Cl and digest with alcohol. { $AuCl_3$. NH_4Cl Evaporate and ignite to Au°, Yellow. $(NH_4)_2PtCl_6$ Ignite to Pt°, Gray.

Blue to green-brown or black solution. } Evaporate to dryness with excess of HNO_3. Dissolve res. in NH_4OH and add to an excess of HCl. Test this sol. with Na_2PHO_4 } Ammonium phosphomolybdate, Yellow.

and test with (*a*) $SnCl_2$ = White $HgCl$ or Gray to Black Hg. (*b*) Au wire = Hg on wire.

y formation of PbI_2 or $PbCrO_4$. See Pb above.

Ppt. $Bi(OH)_3$ Add hot K_2SnO_2 pouring over ppt. on filter. } Bi Black.

Sol. $Cu(OH)_2.2NH_4OH.2NH_4NO_3$ .... $Cd(OH)_2 2NH_4OH.2NH_4NO_3$ | Deep blue solution evidence of copper. For traces add $HC_2H_3O_2$ and test with $K_4Fe(CN)_6$ { $Cu_2Fe(CN)_6$ Red-brown. Add KCN till blue color disappears, then H_2S { CdS Lemon-yellow.

HCl and precipitate with $(NH_4)_2CO_3$ { $Al(OH)_3$ White, gelatinous.

Sol. { K_2CrO_4 and Na_2CrO_4 } Acidify with $HC_2H_3O_2$ and add $Pb(C_2H_3O_2)_2$ { $PbCrO_4$ Lemon-yellow.

Res. $Fe(OH)_3$ } Dissolve in HCl and add KCNS { $Fe(CNS)_3$ Blood red. Test original solution (acid) with KCNS for Fe‴ and with $K_3Fe(CN)_6$ for Fe″ { $Fe_3[Fe(CN)_6]_2$ Blue.

$CoCl_2$ { *a*. Test with borax bead. Blue bead. *c*. Or evaporate $+H_2SO_4$ and add nitroso-β-naphthol. *b*. Add $NaHCO_3$ and H_2O_2, Green solution. Co—Red precipitate. Test with borax bead.

$NiCl_2$ { *a*. Test with borax bead. Brown bead. *c*. Or make sol. ammoniacal and add 1% alcoholic sol. dimethyl-glyoxine = $[(CH_3)_2C_2N_2O_2H]_2Ni$ Red. *b*. Heat with Br and NaOH { $Ni(OH)_3$ } add KI. Free I in CS_2.

$Mn(OH)_2$ { Boil with PbO_2 and HNO_3 } $HMnO_4$. Purple.

Na_2ZnO_2 { Add H_2S } ZnS White. Ppt. is insoluble in dilute acetic acid.

$BaCrO_4$ } Dissolve in HCl and add H_2SO_4 { $BaSO_4$ White.

$Sr(C_2H_3O_2)_2$, $Ca(C_2H_3O_2)_2$ | Add NH_4OH & $(NH_4)_2CO_3$ | $SrCO_3$, $CaCO_3$ | Dissolve in $HC_2H_3O_2$ | $Sr(C_2H_3O_2)_2$, $Ca(C_2H_3O_2)_2$ | Divide into 2 portions: 1. Add $CaSO_4$ set aside 10 minutes { $SrSO_4$ White. Moisten $SrSO_4$ with HCl and apply flame test. 2. Add K_2SO_4, boil, set aside ten minutes. Filter and add $(NH_4)_2C_2O_4$ { CaC_2O_4. White, soluble in HCl.

Precipitate $MgNH_4PO_4$ White.

Solution: K—Apply flame test using cobalt glass. Violet.

Na—After removal of Mg apply flame test, yellow.

NH_4—To the original solution add KOH in strong excess, warm (note odor) and test with moist litmus paper; pass gas into Nessler's reagent K_2HgI_4 sol. { NHg_2I, Brown.

red; (*g*) = green; (*pk*) = pink. Ppt. = precipitate. Res. = residue. Sol. = solution.

GENERAL SUMMARY OF TESTS FOR ACIDS

Acids	Detecting Reagents	Reactions Resulting from Test
Acetates	H_2SO_4 (conc.)	Odor of vinegar
Arsenates	(a) $(NH_4)_2MoO_4+HNO_3$	Yellow precipitate
	(b) Magnesia mixture	White granular precipitate
	(c) Reduced on $C+Na_2CO_3$	Garlic odor, arsenic mirror
Arsenites	(a) Magnesia mixture	No reaction
	(b) H_2S+HCl	Yellow precipitate
Bromides	(a) H_2SO_4 (conc.)	Red Br vapor
	(b) Chlorine water$+CS_2$	Reddish color, due to Br
Borates	H_2SO_4 (conc.)+alcohol	Green flame
Carbonates	Dilute acids	CO_2 evolved. Limewater test
Chlorates	(a) H_2SO_4 (conc.)	Explosive liberation of $Cl+ClO_2$
	(b) Heated alone	O given off
Chlorides	$AgNO_3+HNO_3$	White precipitate, sol. in NH_4OH
Chromates	(a) H_2SO_4 (conc.)	O liberated (sol. yellow to green)
	(b) HCl	Chlorine of HCl liberated
	(a) Alcohol+NaOH	Reduced and $Cr(OH)_3$ precipitated
Cyanides	H_2SO_4 (conc.)	HCN (POISON). Odor, bitter almonds
Ferricyanides	$FeSO_4+HCl$	Turnbull's blue precipitate
Ferrocyanides	$FeCl_3+HCl$	Prussian blue precipitate
Fluorides	H_2SO_4 (conc.)	HF gas liberates silicic acid from glass rod with drop of H_2O
Hypochlorites	Dilute acids	Cl liberated, yellow gas
Iodides	(a) H_2SO_4 (conc.)	Violet vapor of iodine
	(b) Chlorine water$+CS_2$	Violet color to CS_2
Nitrates	$FeSO_4+H_2SO_4$ (conc.)	Brown ring
Nitrites *	Dilute acids	N_2O_3 brown evolved
Oxalates	H_2SO_4 (conc.)	$CO+CO_2$ evolved
Permanganates	Reducing agents	Decolorized
Phosphates	$HNO_3+(NH_4)_2MoO_4$ at 40°	Yellow precipitate
Silicates	(a) Fused with Na_2CO_3 and HCl added	Silicic acid precipitated
	(b) HF	SiF_4 gas liberated
Sulfates	$HCl+BaCl_2$	White precipitate of $BaSO_4$
Sulfides	Dilute acids	H_2S gas blackens $Pb(C_2H_3O_2)_2$
Sulfites	Dilute acids	SO_2 gas
Sulfocyanides	$FeCl_3$	Deep red color
Thiosulfates	Dilute acids	SO_2 gas+free S
Tartrates	Ignited	Char. Odor of burnt sugar
Organic acids	Heated	Generally char

* Nitrites$+KI+CS_2=$ violet color in CS_2 due to free I.

TABLES OF REACTIONS

BASES AND ACIDS

TABLES OF REACTIONS OF THE BASES

HYDROGEN CHLORIDE GROUP

Reagent	Lead, $Pb(NO_3)_2$	Mercury, $HgNO_3$	Silver, $AgNO_3$
Hydrochloric acid, HCl	Lead chloride, $PbCl_2$, white ppt. Slightly sol. in cold water. Solubility in 100 ml. H_2O, 0° = 673 mg. 100° = 3340 mg. Converted into the insol. basic salt by NH_4OH	Mercurous chloride, HgCl, white ppt. Sol. in hot HNO_3 and in aqua regia. NH_4OH converts it to $HgCl \cdot NH_2$ + Hg, black. 100 ml. H_2O dissolves 0.31 mg. (cold), 10 mg. (hot)	Silver chloride, AgCl, white ppt. Insol. in acids. Sol. in NH_4OH, KCN, and $Na_2S_2O_3$. AgCl darkens in the light. Solubility in 100 ml. H_2O, $0.152^{20°}$ mg., $2.2^{100°}$ mg.
Ammonium hydroxide, NH_4OH	$(PbO)_2Pb(NO_3)_2$. Basic salt, white ppt. Insol. in excess. Only slightly sol. in water	Mercuric ammonium salt and mercury, $HgNH_2NO_3$ + Hg, black ppt. Insol. in excess	Silver oxide, AgO, brown ppt. Sol. in excess. Sol. in KCN. $4.3^{20°}$ mg. in 100 ml. H_2O.
Hydrogen sulfide, H_2S	Lead sulfide, PbS, black ppt. Insol. in $(NH_4)_2S_x$. Sol. in HNO_3. Cold water dissolves 0.1 mg. Hot water, insol.	Mercuric sulfide, HgS + Hg, black ppt. Slightly sol. in HNO_3. Sol. in aqua regia. Insol. in water	Silver sulfide, Ag_2S, black ppt. Insol. in $(NH_4)_2S_x$. Sol. in hot HNO_3, 0.02 mg. in cold water. Sol. in conc. H_2SO_4
Potassium chromate, K_2CrO_4	Lead chromate, $PbCrO_4$, yellow ppt. Slightly sol. in HNO_3. Sol. in NH_4OH. Solubility $0.02^{18°}$. Insol. in hot water and in acetic acid	Mercurous chromate, Hg_2CrO_4, brick red. Slightly sol. in HNO_3. Sol. in aqua regia. Sol. in hot water and in KCN	Silver chromate, Ag_2CrO_4, dark red ppt. Sol. in HNO_3 and in NH_4OH. $2.8^{18°}$ mgs. in 100 ml. H_2O. Sol. in KCN

Potassium ferrocyanide, $K_4Fe(CN)_6$	Lead ferrocyanide, $Pb_2Fe(CN)_6$, white ppt. Insol. in cold water	Mercurous ferrocyanide, $Hg_4Fe(CN)_6$, white ppt.	Silver ferrocyanide, $Ag_4Fe(CN)_6$, yellowish white ppt. Insol. in acids and in NH_4OH. Sol. in KCN
Sodium carbonate, Na_2CO_3	Basic lead carbonate, $2\ PbCO_3 \cdot Pb(OH)_2$, white ppt., "white lead." Insol. in hot and cold water	Basic salt, yellow ppt., becoming black	Silver carbonate, Ag_2CO_3, white ppt. Sol. in NH_4OH, $3.1^{15°}$, 50 mg. at 100° in H_2O. Sol. in $Na_2S_2O_3$
Sodium hydroxide, NaOH	Lead hydroxide, $Pb(OH)_2$, white ppt. Sol. in excess. Sol. in HNO_3. Insol. in NH_4OH. Sol. in KOH. Slightly sol. in water	Mercurous oxide, Hg_2O, black ppt. Sol. in HNO_3. Insol. in NH_4OH and alkalies. Sol. in glacial acetic acid	Silver oxide, Ag_2O, brown ppt. Sol. in NH_4OH and in HNO_3. 4.3 mg. at 20° in H_2O. Sol. in KCN
Stannous chloride, $SnCl_2$	Lead chloride, $PbCl_2$. Sol. in hot water (See above)	Mercury, Hg, dark gray ppt. Sol. in HNO_3, conc. H_2SO_4. Insol. in HCl	Silver chloride, AgCl, white ppt. (See above)
Sulfuric acid, H_2SO_4	Lead sulfate, $PbSO_4$, white ppt. Insol. in excess. Slightly sol. in HNO_3. Sol. in NaOH, $NH_4C_2H_3O_2$. 4.2 at 20°	Mercurous sulfate, Hg_2SO_4, white ppt. Slightly sol. in water, 200 mg. Sol. in H_2SO_4, HNO_3	Silver sulfate, Ag_2SO_4, white ppt. Formed only in conc. solutions. Insol. in alkalies. Sol. in H_2SO_4 and in HNO_3. 580 mg. in H_2O
Miscellany	Zn ppts. Pb in crystalline form. Pb sol. in HNO_3. Hot conc. H_2SO_4	Pptd. in acid solutions by Cu, Zn, from its salts as metallic Hg. SO_2 reduces mercurous salts to Hg, which collects as globules on boiling solution. Hg sol. in HNO_3. Insol. in HCl	Insoluble salts, AgBr, AgI. Ag is displaced from its salts in crystalline form by Zn, Cu, Hg, and in gray form by SO_2, $SnCl_2$, $FeSO_4$, etc. Ag sol. in HNO_3. Insol. in alkalies

The numerals indicate milligrams of the substance that will dissolve in 100 ml. of water at stated temperature. Reference to Van Nostrand's Chemical Annual, edited by Olsen.

THE HYDROGEN SULFIDE GROUP

Insoluble Subgroup

Sol. = Soluble. Insol. = Insoluble.

Reagent	Bismuth, $BiCl_3$	Cadmium, $CdSO_4$	Copper, $CuSO_4$	Mercury (= ic), $HgCl_2$
Hydrogen sulfide, H_2S	Bismuth sulfide, Bi_2S_3, brown ppt. Sol. in HNO_3. Insol. in $(NH_4)_2S_x$ and in KCN. Cold water 100 ml. dissolves 0.018 mg.	Cadmium sulfide, CdS, yellow ppt. Sol. in HNO_3, H_2SO_4 (hot dil.). Insol. in $(NH_4)_2S_x$, KCN. Cold H_2O, 0.13 mg. Hot H_2O forms colloidal solution	Copper sulfide, CuS, black ppt. Sol. in HNO_3, KCN. Slightly sol. in $(NH_4)_2S_x$. Insol. in H_2SO_4 (hot dil.). Cold H_2O, 0.033 mg.	Mercuric sulfide, HgS, white → yellow → red → brown → black. Insol. in HNO_3, $(NH_4)_2S_x$. Sol. in Br + $KClO_3$ or aqua regia, Na_2S. Cold H_2O, 2.5 mg.
Ammonium hydroxide, NH_4OH	Bismuth hydroxide, $Bi(OH)_3$, white ppt. Insol. in excess. Changed by boiling to Bi_2O_3. Insol. in H_2O. Insol. in alkalies	Cadmium hydroxide, $Cd(OH)_2$, white ppt. Sol. in excess. Insol. in water, e.g. $0.26^{25°}$ mg. Sol. in NH_4 salts	Basic copper, ammonium sulfate. Sol. in excess = a deep blue. $Cu(NH_3)_4 \cdot SO_4'' \cdot H_2O$, characteristic test	Amido mercuric chloride, $HgNH_2Cl$, white ppt.
Potassium chromate, K_2CrO_4	Bismuth chromate, $(BiO)_2CrO_4$, yellow ppt. Sol. in HNO_3. Insol. in KOH (See Pb)	Basic chromate, $Cd_2(OH)_2CrO_4$, yellow. Insol. in NaOH	Copper chromate, $CuCrO_4$, reddish brown ppt. Sol. in NH_4OH, forming a green solution	Mercuric chromate, $HgCrO_4$, reddish yellow ppt. Sol. in HNO_3. Slightly sol. in water
Potassium cyanide, KCN		Cadmium cyanide, $Cd(CN)_2$, white ppt. Sol. in excess = $Cd(CN)_2(KCN)_2$. From this H_2S ppts. CdS, yellow	Copper cyanide, $Cu(CN)_2$, greenish yellow ppt. Sol. in excess = $Cu(CN)_2(KCN)_2$. No pptn. by H_2S	$Hg(CN)_2$. Sol. in water. 12500 mg.

Potassium ferrocyanide, $K_4Fe(CN)_6$	Bismuth ferrocyanide, $Bi_4(Fe(CN)_6)_3$, white ppt. Insol. in HCl	Cadmium ferrocyanide, $Cd_2Fe(CN)_6$, yellowish white ppt. Sol. in HCl. Insol. in H_2O	Copper ferrocyanide, $Cu_2Fe(CN)_6$, reddish brown pp. Slightly sol. in NH_4OH. Insol. in acids	
Sodium carbonate, Na_2CO_3	Basic bismuth carbonate, $(BiO)_2CO_3$, white ppt. Insol. in water. Sol. in acids. Insol. in Na_2CO_3	Cadmium carbonate, $CdCO_3$, white ppt. Insol. in excess. Sol. in NH_4OH. Sol. in acids	Basic copper carbonate, $Cu_2(OH)_2CO_3$, blue. Changed to black CuO on boiling	Mercuric basic carbonate, $HgCO_3(HgO)_3$, reddish brown ppt. Changed to yellow HgO on boiling. Insol. in H_2O
Sodium hydroxide, NaOH	Bismuth hydroxide, $Bi(OH)_3$, white ppt. See above	Cadmium hydroxide, $Cd(OH)_2$, white ppt. Insol. in excess (See above)	Copper hydroxide, $Cu(OH)_2$, light blue. Insol. in excess. Changed to black CuO on boiling	Mercuric hydroxide, $Hg(OH)_2$. Easily changed to HgO, yellow. Insol. in excess. In presence of NH_4Cl = $HgNH_2Cl$, white ppt.
Sulfuric acid, H_2SO_4	* No precipitate	No precipitate	No precipitate	No precipitate
Stannous chloride, $SnCl_2$	Darkens. Precipitate of BiOOH changes to Bi_2O_3		Cuprous chloride, CuCl, white ppt. Sol. in HCl, NH_3 aq., NH_4Cl. Insol. in H_2O	Mercurous chloride, HgCl, white ppt. In excess = gray, Hg
Miscellany	In water Bi salt precipitates as BiOCl, white. Reduced by Na_2SnO_2 to metallic Bi, black. Bi sol. in HNO_3, conc. H_2SO_4	Na_2HPO_4 ppts. $Cd_3(PO_4)_2$, white. Sol. in NH_4OH and in dilute acids. Cd sol. in acids. Sol. in NH_4NO_3	Na_2HPO_4 precipitates $Cu_3(PO_4)_2$, greenish blue. Sol. in NH_4OH. KI ppts. Cu_2I_2, white + I = brown. Cu sol. in HNO_3, hot conc. H_2SO_4	Precipitated by Cu. KI ppts. HgI_2, red. Sol. in excess. Hg sol. in HNO_3, conc. H_2SO_4. Insol. in HCl

* A precipitate forms on long standing.

THE SOLUBLE H_2S

	ARSENIC, As''', As'''''		ANTIMONY, Sb''', Sb'''''	
	(ous) K_3AsO_3	(ic) KH_2AsO_4	(ous) $SbCl_3$	(ic) $KSbO_3$
Hydrogen sulfide, H_2S	Arsenic trisulfide, As_2S_3, yellow ppt. Sol. in alkalies, $(NH_4)_2S_x$, $(NH_4)_2S$. Insol. in conc. HCl	Arsenic trisulfide+S, and As_2S_5, yellow. The ppt. forms slowly by heat	Antimony trisulfide, Sb_2S_3, orange ppt. Sol. in alkalies, $(NH_4)_2S_x$, $(NH_4)_2S$, HCl (conc.). 0.17 mg.	Antimony pentasulfide, Sb_2S_5, orange ppt. Sol. in alkalies, $(NH_4)_2S_x$, $(NH_4)_2S$, HCl (conc.)
Ammonium hydroxide, NH_4OH			Antimonious hydroxide, $Sb(OH)_3$, white ppt. Sol. in excess	Ammonium metantimonate, NH_4SbO_3. Very slightly sol. in excess
Copper sulfate, $CuSO_4$	Copper arsenite, $CuHAsO_3$, yellowish green ppt. Sol. in NH_4OH, NaOH, HNO_3	Copper arsenate, $Cu_3(AsO_4)_2$, greenish blue ppt. Sol. in NH_4OH and in HNO_3	Antimony oxychloride, white, SbOCl, caused by dilution. Insol. alk Sol. HCl, CS_2	Copper antimonate, brown ppt.
Mercuric chloride, $HgCl_2$	Mercuric arsenite, $Hg_3(AsO_3)_2$, white ppt. Sol. in acids		Antimony oxychloride, caused by dilution. Sol. in conc. HCl	
Silver nitrate, $AgNO_3$	Silver arsenite, Ag_3AsO_3, yellow ppt. Sol. in HNO_3, NH_4OH, $HC_2H_3O_2$	Silver arsenate, Ag_3AsO_4, reddish brown ppt. Sol. in HNO_3 and NH_4OH	Silver chloride and antimony trioxide, $AgCl+Sb_2O_3$, white ppts.	Silver antimonate, $AgSbO_3$, white ppt. Sol. in NH_4OH
Miscellany	Magnesia mixture. No ppt. Arsenic sol. in HNO_3, Cl_2, H_2O, aq. reg., hot alkalies	Magnesia mixture ppts. $MgNH_4AsO_4$, white crys. ppt. Sol. in acetic acid.	KOH ppts. $Sb(OH)_3$. Na_2CO_3 ppts. $Sb(OH)_3$	Sb. sol. in hot conc. H_2SO_4 and in aq. reg.
	Marsh test (Zn+HCl, etc.)	AsH_3 flame deposits arsenic. Sol. in NaOCl. Sol. in $(NH_4)_2S$. Residue insol. in HCl (conc.)	Marsh test (Zn+HCl)	SbH_3 in flame deposits antimony. Insol. in NaOCl

† See Van Nostrand's Chemical Annual for solubility of salts.

SUBGROUP

TIN, Sn¨, Sn''''		PLATINUM, Pt''''	GOLD, Au'''
(ous) $SnCl_2$	(ic) $SnCl_4$	$PtCl_4$	$AuCl_3$
Stannous sulfide, SnS, dark brown. Sol. in alkalies. Difficultly sol. in $(NH_4)_2S_x$. Sol. in HCl (conc.). 100 ml. H_2O diss. 0.002 mg.	Stannic sulfide, SnS_2, yellow ppt. Sol. in alkalies, $(NH_4)_2S_x$, $(NH_4)_2S$ and alkali carbonates. HCl (conc.). $H_2O = 0.02$ mg.	Platinic sulfide, PtS_2, dark brown ppt. Difficultly sol. in alkali sulfides. Sol. in aqua regia. Insol. in HCl (conc.)	Gold sulfide, Au_2S_3, black ppt. Sol. in alkali sulfides, aqua regia. Insol. in HCl (conc.)
Stannous hydroxide, $Sn(OH)_2$. Insol. in excess. Darkens on standing. Insol. in H_2O. Sol. in dilute acids, alk.	Stannic hydroxide, $Sn(OH)_4$. Slightly sol. in excess	Ammonium chloroplatinate, $(NH_4)_2PtCl_6$, yellow ppt. Sol. in large excess. $679^{20°}$ mg.	Fulminating gold, Au_2O_3. 2 NH_3, yellow ppt., insol. in excess
Cuprous chloride, 2 CuCl, white ppt. Sol. in acids. Reduction by $SnCl_2$			
Mercurous chloride, HgCl, white ppt. Insol. in cold HCl (conc.). Reduction by $SnCl_2$			
Silver chloride and silver, AgCl+Ag. Reduction by $SnCl_2$	Silver chloride, AgCl	Silver chloride and platinum oxide, AgCl+PtO, brown ppt.	Silver chloride and gold oxide, $AgCl+Au_2O_3$, brown ppt.
KOH ppts. $Sn(OH)_2$, Na_2CO_3 ppts. $Sn(OH)_2$. Insol. in excess	KOH ppts. $Sn(OH)_2$. $NaCO_3$ ppts. $Sn(OH)_2$. Insol. in excess	KOH ppts. K_2PtCl_6. Na_2CO_3 gives no ppt. Pt sol. in aq. r., fused alk.	$SnCl_2$ solution ppts. "Purple of Cassius," red ppt. Au sol. in KCN, aq. reg.
Metallic Sn deposited by Zn in Marsh test	Stannic salts reduced by H, generated by Sn	Zn ppts. Pt, black, from its salts. Also see Electromotive Series, p. 1141	Zn ppts. Au from its salts

THE AMMONIUM SULFIDE GROUP

Numbers refer to mgs. soluble in 100 ml. cold water

Reagent	Aluminum, $Al^{\cdots}$	Chromium, $Cr^{\cdots}$	Iron, $Fe^{\cdot\cdot}$	$Fe^{\cdots}$
	$Al_2K_2(SO_4)_4$	$Cr_2K_2(SO_4)_4$	Ferrous, $FeSO_4$	Ferric, $FeCl_3$
Ammonium sulfide, $(NH_4)_2S$	Aluminum hydroxide, $Al(OH)_3$, white flocculent ppt. Sol. in acids. H_2S gas liberated	Chromium hydroxide, $Cr(OH)_3$, grayish green, ppt. H_2S liberated. Sol. in acids and alkalies	Iron sulfide, FeS, black ppt. sol. in acids. Oxidizes in the air to $FeSO_4$ and finally to a brown basic ferric sulfate. 0.89 mg.	Iron sulfide, FeS(+S), black ppt. Sol. in acids. S remains undissolved
Ammonium hydroxide, NH_4OH	Aluminum hydroxide, $Al(OH)_3$, white. Very slightly sol. in excess of reagent	Chromium hydroxide, $Cr(OH)_3$, grayish green. Slightly sol. in excess, forming a reddish solution when cold and concentrated	Ferrous hydroxide, white ppt. becoming green, then reddish brown, in the air and in presence of NH_4Cl. $Fe(OH)_3$ slowly forms. Sol. in NH_4Cl. 6.7 mgs.	Ferric hydroxide, $Fe(OH)_3$, reddish brown ppt. Insol. in excess of reagent
Ammonium carbonate, $(NH_4)_2CO_3$	Aluminum hydroxide, $Al(OH)_3$, white ppt. CO_2 gas	Chromium hydroxide, $Cr(OH)_3$, grayish green. Sol. in excess of reagent CO_2 liberated	Ferrous carbonate, $FeCO_3$, white ppt. sol. in excess. Slowly changed to hydroxide	Basic salt changing to $Fe(OH)_3$, reddish brown ppt.
Barium carbonate, $BaCO_3$	Aluminum hydroxide, $Al(OH)_3$, white	Basic salt, CO_2, liberated, and $Cr(OH)_3$ formed	Iron not pptd. in ferrous form by $BaCO_3$	Same as above
Borax bead, $Na_2B_4O_7 \cdot 10\ H_2O$		OF, yellowish green when hot, changing to emerald-green, cold	OF, yellow. RF, green	OF, yellow. RF, green
Hydrogen sulfide, H_2S			In presence of sodium acetate, FeS pptd.	$Fe^{\cdots}$ reduced to $Fe^{\cdot\cdot}$ with liberation of free S. (Also reduced by $SnCl_2$)

Potassium ferricyanide, $K_3Fe(CN)_6$		(All Cr compounds oxidized to compounds of chromic acid; e.g. $2\ Na_2CO_3 + 3\ KNO_3 + 2\ Cr(OH)_3 = 2\ Na_2CrO_4 +$ etc.)	Ferrous ferricyanide (Turnbull's blue), $Fe_3(FeC_6N_6)_2$, dark blue ppt. Insol. in HCl. Decomposed by NaOH to $Fe(OH)_2$	Reddish brown color produced
Potassium ferrocyanide, $K_4Fe(CN)_6$	White ppt. forms slowly		Potassium ferrous ferrocyanide, $K_2Fe_3(FeC_6N_6)_2$, bluish white, oxidized in air to blue	Ferric ferrocyanide, $Fe_4(FeC_6N_6)_3$, (Prussian blue), dark blue. Insol. in mineral acid. NaOH forms $Fe(OH)_3$
Sodium hydroxide, NaOH	‡ Aluminum hydroxide, $Al(OH)_3$, white. Sol. in excess, forming $Na^{\cdot}{}_3 \rightarrow AlO_3'''$. ($NaAlO_2$). Repptd. by NH_4Cl	‡ Chromium hydroxide, $Cr(OH)_3$, greenish ppt. Sol. in excess, forming green solution $NaCrO_2$. Repptd. by boiling or by addition of NH_4Cl	‡ Ferrous hydroxide, $Fe(OH)_2$, white becoming $Fe(OH)_3$. Insol. in excess. Non-volatile organic substance prevents pption.	‡ Ferric hydroxide, $Fe(OH)_3$, reddish brown ppt. Insol. in excess. Sol. in mineral acids
Sodium phosphate, Na_2HPO_4	$AlPO_4$, white. Sol. in NaOH. Insol. in $HC_2H_3O_2$	$CrPO_4$, green ppt. Sol. in mineral acids and in NaOH	$Fe_3(PO_4)_2$, white ppt. becoming blue in the air	$FePO_4$, yellowish white, sol. in excess. Insol. in $HC_2H_3O_2$
Miscellany	Sodium acetate in excess boiled with Al salt ppts. basic $Al(OH)_2(C_2H_3O_2)$ in neutral solutions	$NaC_2H_3O_2$ forms no ppt. unless Fe and Al are present, in which case Cr partially pptd. by boiling	KCNS, no color. KCN ppts. $Fe(CN)_2$, brown. Sol. in excess	KCNS = red $Fe(SCN)_3$. Boiling with $NaC_2H_3O_2$ in neutral solutions a red brown ppt. formed of $(FeOH)_2(C_2H_3O_2)$

‡ Presence of non-volatile organic substances, tartrates, citrates, and sugar prevents precipitation.

THE AMMONIUM SULFIDE GROUP—*Continued*

Reagent	Cobalt, $CoCl_2$	Nickel, $NiCl_2$	Manganese, $MnSO_4$	Zinc, $ZnSO_4$
$(NH_4)_2S$	Cobalt sulfide, CoS, black ppt. Insol. in $HC_2H_3O_2$. Very slightly sol. in HCl. Sol. in aqua regia and warm HNO_3. 0.38 mg.	Nickel sulfide, NiS, black ppt. Slightly sol. in excess, forming a brown solution. Very slightly sol. in HCl. Sol. in aqua regia. 0.36 mg.	Manganese sulfide, MnS, buff-colored ppt. Sol. in HCl, $HC_2H_3O_2$. Oxidizes in the air. 0.6 mg.	Zinc sulfide, ZnS, white ppt. Insol. in $HC_2H_3O_2$. Sol. in HCl. Presence of NH_4Cl aids pption.
NH_4OH	Blue basic salt, sol. in excess, forming red solution. No ppt. formed in presence of NH_4Cl. Solution becomes red	Nickel hydroxide, $Ni(OH)_2$, green ppt. Sol. in excess, forming a blue solution. No ppt. formed in presence of NH_4Cl	Manganese hydroxide, $Mn(OH)_2$, white ppt. turning brown. In presence of NH_4Cl a dark brown ppt. slowly forms by oxidation, $Mn(OH)_3$	Zinc hydroxide, $Zn(OH)_2$, white ppt. Sol. in excess, $ZnSO_4(NH_3)_4$ formed. In presence of NH_4Cl no ppt. forms
$(NH_4)_2CO_3$	Basic carbonate, red, lilac, or pink ppt. Sol. in excess, forming red solution, becoming brown by air oxidation	Basic carbonate of variable compositions, green ppt. Sol. in excess	Manganese carbonate, $MnCO_3$, white ppt. Sol. in excess. Boiling aids pption.	Basic zinc carbonate, usually $Zn_3(OH)_2CO_3$, white ppt. Sol. in excess (Acid carbonate ppts. $ZnCO_3$ white)
$BaCO_3$	No ppt. in cold	No ppt. in cold	No ppt. in cold	No pption. in cold. (Na_2CO_3 ppts. above aided by boiling)
Borax bead	Blue	Violet, hot. Yellowish brown, cold	OF, violet-red, hot. Amethyst-red, cold. RF, colorless	
H_2S	From neutral or alkaline solutions, CoS, black. No ppt. in acid solutions	From neutral or alkaline solutions, NiS. No ppt. in acid solutions	MnS forms slowly from alkaline solutions. No ppt. in acid solutions	From neutral or alkaline solutions, or in solutions acidified with $HC_2H_3O_2$, ZnS is pptd.

$K_3Fe(CN)_6$	Cobalt ferricyanide, $Co_3(FeC_6N_6)_2$, dark brown ppt. Insol. in HCl	Nickel ferricyanide $Ni_3(FeC_6N_6)_2$, yellowish green ppt. Insol. in HCl	Manganese ferricyanide, $Mn_3(FeC_6N_6)_2$, brown ppt. Insol. in HCl	Zinc ferricyanide, $Zn_3(FeC_6N_6)_2$, yellowish brown ppt. Sol. in HCl and in NH_4OH
$K_4Fe(CN)_6$	Cobalt ferrocyanide, $Co_2Fe(CN)_6$, green ppt. becoming greenish blue. Insol. in HCl. Sol. in KCN	Nickel ferrocyanide, $Ni_2Fe(CN)_6$, light green ppt. Insol. in HCl	Manganese ferrocyanide, $Mn_2Fe(CN)_6$, faint red ppt. Diff. sol. in HCl. Easily sol. in H_2SO_4, HNO_3	Zinc ferrocyanide, $Zn_2Fe(CN)_6$, white ppt. Insol. in dilute acids and in NH_4OH
NaOH	Basic salt, blue. Boiled with excess = red. Insol. in excess. Sol. in $HC_2H_3O_2$, HCl, NH_4OH	Nickel hydroxide, $Ni(OH)_2$, apple green ppt. Insol. in excess. Sol. in $HC_2H_3O_2$, HCl, NH_4OH. Oxidized by Br to $Ni(OH)_3$	Manganese hydroxide, $Mn(OH)_2$, white ppt. turning brown. Insol. in excess. Sol. in NH_4Cl	Zinc hydroxide, $Zn(OH)_2$, white ppt. Sol. in excess, forming Na_2ZnO_2. Repptd. by boiling
Na_2HPO_4	$Co_3(PO_4)_2$, blue ppt. Sol. in NH_4OH. Col. in dil. acids. Sol. in H_3PO_4	$Ni_3(PO_4)_2$, green ppt. Sol. in NH_4OH. Sol. in dil. acids	$Mn_3(PO_4)_2$, white ppt. Sol. in NH_4OH, mineral acids, and $HC_2H_3O_2$. Boiled with $NH_4OH + NH_4Cl = MnNH_4PO_4$, rose colored	$Zn_3(PO_4)_2$, white ppt. Sol. in excess and in dil. acids and in NH_4OH
Miscellany	HCN ppts. reddish brown, $Co(CN)_2$. Sol. in excess. Addition of Br+NaOH $= K_3Co(CN)_6$. Co not pptd. (Ni is pptd.)	HCN ppts. greenish yellow, $Ni(CN)_2$. Sol. in excess. Repptd. by HCl. Pptd. by Br+NaOH as $Ni(OH)_3$, black+CNBr (poison gas)	$PbO_2 + HNO_3 +$ Mn salt warmed = red $HMnO_4$. $Na_2CO_3 + KNO_3$ fused on Pt = green, Na_2MnO_4	KCN ppts. $Zn(CN)_2$, white. Sol. in excess. From this solution $(NH_4)_2S$ ppts. ZnS, white

For solubility of salts, see tables in D. Van Nostrand's *Chemical Annual*, edited by Olsen.

THE AMMONIUM CARBONATE GROUP

Solubility in milligrams per 100 ml. of water cold, "c," and hot, "h"

Reagent	Barium, $BaCl_2$	Calcium, $CaCl_2$	Strontium, $SrCl_2$	Soluble in Presence of NH_4 Salts. Magnesium, $MgSO_4$
Ammonium carbonate, $(NH_4)_2CO_3$	Barium carbonate, $BaCO_3$, white ppt. Sol. in acids. Slightly sol. in NH_4Cl. Precipitation aided by excess of NH_4OH and by boiling. "c" 2.2 mg.; "h" 6.5 mg.	Calcium carbonate, $CaCO_3$, white ppt. Sol. in acids. Slightly sol. in NH_4Cl. Rendered less sol. by boiling with NH_4OH. "c" 1.3 mg.; "h" 88 mg.	Strontium carbonate, $SrCO_3$, white ppt. Sol. in acids. Slightly sol. in NH_4Cl. Rendered less sol. by boiling with excess of NH_4OH. "c" 1.1 mg.	Basic magnesium carbonate $MgCO_3+Mg(OH)_2$, white ppt. on warming. No ppt. formed if NH_4 salts are present. But if absent, solubility only 10.6 mgs.
Ammonium hydroxide, NH_4OH				Magnesium hydroxide, $Mg(OH)_2$. Sol. in NH_4Cl
Ammonium oxalate, $(NH_4)_2C_2O_4$	Barium oxalate, BaC_2O_4, white ppt. Sol. in HCl. Slightly sol. in $HC_2H_3O_2$ and water. "c" 9.3; "h" 22.8	Calcium oxalate, CaC_2O_4 white ppt. Sol. in HCl. Almost insol. in $HC_2H_3O_2$ or in $H_2C_2O_4$. "c" 0.68 mg.; "h" 1.4 mg.	Strontium oxalate, SrC_2O_4, white ppt. Sol. in HCl. Slightly sol. in $HC_2H_3O_2$ and water. "c" 5.1 mg. Sol. in hot solutions	
Ammonium sulfate, $(NH_4)_2SO_4$, or sulfuric acid, H_2SO_4	Barium sulfate, $BaSO_4$, white ppt. Insol. in H_2O and in acids. "c" 0.17 mg.; "h" 0.3 mg.	Calcium sulfate, white ppt. Somewhat sol in H_2O. Sol. in $(NH_4)_2SO_4$. Insol. in alcohol. "c" 179 mg.; "h" 178 mg.	Strontium sulfate, $SrSO_4$, white ppt. Slightly sol. in H_2O and in $(NH_4)_2SO_4$. "c" 11.4 mg.; "h" 10.4 mg.	

Potassium chromate, K_2CrO_4	Barium chromate, $BaCrO_4$, yellow ppt. Insol. in $HC_2H_3O_2$ in presence of K_2CrO_4. Sol. in HCl. HNO_3. "c" 0.38 mg.; "h" 4.3 mg.			
Sodium hydroxide, NaOH	Barium hydroxide, $Ba(OH)_2$, white ppt. formed only in conc. solutions. "c" 5560 mg.; "h" very soluble	Calcium hydroxide, $Ca(OH)_2$, white ppt. Difficulty sol. in water. Sol. in NH_4Cl. "c" 170 mg.; "h" 80 mg.	Strontium hydroxide, $Sr(OH)_2$, white ppt. Slightly sol. in water; "c" 410 mg.; "h" very soluble	Magnesium hydroxide, $Mg(OH)_2$, white ppt. Sol. in NH_4Cl
Sodium phosphate, Na_2HPO_4	Barium hydrogen phosphate, $BaHPO_4$, white ppt. "c" 10–20 mg. Sol. in acids. If NH_4OH present, $BaNH_4PO_4$ formed	Calcium hydrogen phosphate, $CaHPO_4$, white ppt. "c" = 28 mg. Sol. in acids. In presence of NH_4OH, $Ca_3(PO_4)_2$ pptd. "c" 3 mg to 8 mg	Strontium hydrogen phosphate, $SrHPO_4$, white ppt. Sol. in acids. See $BaHPO_4$ Insol in H_2O	Magnesium hydrogen phosphate, $MgHPO_4$, white ppt. Boiled = $Mg_3(PO_4)_2$. In presence of NH_4Cl and NH_4OH a white crystalline ppt. of $MgNH_4PO_4$ slowly forms. Sol. in acetic acid
Flame	Yellowish green	Yellowish red	Crimson	White
Spectra	Green α and β bands. Fainter yellow and red bands	Sharp orange line α and bluish line β	Several orange and red lines. Brilliant blue line	
Miscellany	H_2SiF_6 ppts. $BaSiF_6$ Insol in alcohol and dilute acids. "c" 26 mg.; "h" 90 mg.	No ppt. by H_2SiF_6	No ppt. by H_2SiF_6	No ppt. by H_2SiF_6. Boiled with Na_2CO_3 = white $Mg_3(OH)_2(CO_3)_2$. No ppt. if NH_4Cl present

THE SOLUBLE METAL GROUP

Reagent	Ammonium, NH_4Cl	Lithium, LiCl	Potassium, KCl	Sodium, NaCl
Hydrofluosilicic acid, H_2SiF_6			Potassium fluosilicate, K_2SiF_6. Transparent ppt. Slightly sol. in water. "c" = 120 mg.; "h" 955 mg.	Sodium fluosilicate, Na_2SiF_6, white ppt. Somewhat sol. in water. "c" = 650 mg.; "h" 2460 mg.
Nessler's reagents, $HgI_2(KI)_2$. KOH	Reddish brown or yellow, according to amount of ammonia. Test very delicate			
Platinic chloride, $PtCl_4$. H_2PtCl_6	Ammonium chloroplatinate, $(NH_4)_2PtCl_6$, yellow ppt. Slightly sol. in water. Insol. in alcohol. "c" 670.0 mg. Very sol. in hot water		Potassium chloroplatinate, K_2PtCl_6, yellow ppt. Slightly sol. in water. Insol. in alcohol or ether. "c" 480 mg.; "h" 5180 mg.	
Potassium pyroantimonate, $H_2K_2Sb_2O_7$				Sodium pyroantimonate, $Na_2H_2Sb_2O_7$, white cryst. ppt. Best formed in slightly alkaline solutions. $NaSbO_3$+aqua. "c" = 31 mg.

Sodium carbonate, Na_2CO_3	Ammonia gas evolved on boiling	Lithium carbonate, Li_2CO_3, white ppt. Slightly sol. in water. Less sol. in hot than in cold. "c" = 1539 mg.; "h" 728 mg.		
Sodium cobaltic nitrite $Co(NO_2)_3 \cdot 3\,NaNO_2$	In acetic acid solutions (see Na), $Co(NO_2)_3 \cdot 3\,NH_4NO_2$, yellow ppt. Sol. in inorganic acids		Potassium cobalt nitrite, $K_3Co(NO_2)_6$, yellow, or $K_2NaCo(NO_2)_6$ in presence of an excess of sodium. Insol. in acetic acid. Sol. in inorganic acids. Hastened by warming. Solution should have acetic acid present. 70 mg. 25°	No ppt. in acetic acid solutions of sodium salts
Sodium or potassium hydroxide, NaOH or KOH	Ammonia gas evolved when salt is warmed with NaOH or KOH			
Sodium phosphate, Na_2HPO_4		Lithium phosphate, Li_3PO_4, white ppt. Slightly sol. in water. Sol. in HCl. "c" = 40 mg.		
Tartaric acid, $H_2C_4H_4O_6$	Monoammonium tartrate, $NH_4HC_4H_4O_6$, white cryst. ppt. Hastened by shaking. Slightly sol. in H_2O		Monopotassium tartrate, $KHC_4H_4O_6$, white cryst. ppt. Hastened by stirring. Somewhat sol. in H_2O. "c" 370 mg.	
Flame and spectrum		Red flame. Bright crimson line with feeble orange line	Violet flame. A red and blue line	Yellow flame. Single yellow line

REACTIONS OF THE ACIDS

INORGANIC ACIDS

Acids / Reagents	Silver Nitrate, $AgNO_3$	Barium Chloride, $BaCl_2$	Calcium Chloride, $CaCl_2$	Lead Acetate, $Pb(C_2H_3O_2)_2$	Characteristic Reactions
Arsenic, H_3AsO_4, arsenates	Reddish brown ppt., Ag_3AsO_4. Sol. in NH_4OH, HNO_3	White ppt., $Ba_3(AsO_4)_2$. Sol. in acids	White ppt. $Ca_3(AsO_4)_2$. Sol. in acetic acid	Lead acetate ppts. white salt. Insol. in acetic acid. Sol. in HNO_3	$(NH_4)_2MoO_4$ produces a yellow ppt. $MgSO_4+NH_4Cl+NH_4OH$ = white ppt.
Arsenious, H_3AsO_3, arsenites	Yellow ppt., Ag_3AsO_3. Sol. in NH_4OH, HNO_3	White ppt., $Ba_3(AsO_3)_2$. Sol. in acids	White ppt. Sol. in $C_2H_4O_2$	Lead acetate ppts. white arsenious salt. Sol. in acetic acid, HNO_3	Marsh's test with both forms—-ous and -ic—gives arsenic mirror. Sol. in NaOCl. H_2S produces yellow As_2S_3 and As_2S_5. Gutzeit test
Boric, H_3BO_3, $(H_2B_4O_7)$, borates	White ppt. Sol. in NH_4OH, HNO_3	White ppt. Not readily sol. in water. Sol. in acids	White ppt. Sol. in acids	White ppt. Caused by lead acetate. Sol. in excess	$H_2SO_4+C_2H_5OH$ colors flame green. Turmeric paper dipped in boric acid salt acidified with HCl, dried, turns red
Carbonic, H_2CO_3, carbonates	Grayish white ppt., Ag_2CO_3. Sol. in HNO_3. $3.1^{15°}$ mg.	White ppt., $BaCO_3$. Sol. in acids. 22 mg.	White ppt., $CaCO_3$. Sol. in acids. 2.2 mg.	Lead acetate ppts. white lead. Sol. in HNO_3	Effervesces with dilute inorganic acids, HCl, H_2SO_4, HNO_3, etc., CO_2 gas being evolved. Limewater clouded by CO_2, $CaCO_3$ being formed

Chloric, $HClO_3$, chlorates				H_2SO_4, conc., warmed with salt causes explosion	Heated on charcoal deflagrates. H_2SO_4 evolves yellow gas, ClO_2
Chromic, H_2CrO_4, chromates	Dark red ppt., Ag_2CrO_4. Sol. in HNO_3. $2.8^{18°}$ mg.	Yellow ppt., $BaCrO_4$. Sol. in HCl, HNO_3. Insol. in acetic acid. 0.38 mg.		$Pb(C_2H_3O_2)_2$ ppts. yellow $PbCrO_4$. Sol. in NaOH. $0.02^{85°}$ mg.	Reduced to green $CrCl_3$ by warming with alcohol and HCl
Hydroiodic, HI, iodides	Yellow ppt., AgI_2. Very difficultly sol. in NH_4OH. $0.035^{21°}$ mg.			Soluble lead salt ppts. PbI_2, yellow. Sol. in hot water. 39,000 mg.	Liberated from its salts by HNO_3, or Cl water. Imparts in free form violet color to CS_2, blue to starch
Hydrobromic, HBr, bromides	Light yellow ppt., AgBr. Difficultly sol. in NH_4OH			$Pb(C_2H_3O_2)_2$ ppts. $PbBr_2$, white. Sol. in hot water. 455 mg.	Liberated from its salts by Cl_2, colors CS_2 reddish yellow

INORGANIC ACIDS

Acids	$AgNO_3$	$BaCl_2$	$CaCl_2$	$Pb(C_2H_3O_2)_2$	Characteristic Reactions
Hydrochloric, HCl, chlorides	White ppt., $AgCl$. Insol. in HNO_3. Sol. in NH_4OH, KCN. 0.152 mg.			$PbCl_2$, white, is pptd. Sol. in hot water. Insol. in alcohol. 673 mg.	$K_2Cr_2O_7+H_2SO_4$, (conc.), gives CrO_2Cl_2. $MnO_2+H_2SO_4$ gives Cl gas. $KMnO_4+HCl$ evolves Cl
Hydrocyanic, HCN, cyanides	White ppt., $AgCN$. Sol. in NH_4OH, KCN. 0.021 mg.			White ppt. with sol. Pb salt, $Pb(CN)_2$. Sol. in HNO_3	Warmed with $NaOH+FeSO_4+FeCl_3$ and acidified with HCl, "Prussian Blue" formed. Warmed with $(NH_4)_2S_x=NH_4CNS$, which produces a blood-red color with $FeCl_3$
Hydroferricyanic, $H_3Fe(CN)_6$, ferricyanides	Orange ppt., $Ag_3Fe(CN)_6$. Sol. in NH_4OH, KCN. Insol. in HNO_3			On warming, PbO_2 is pptd.	Dark blue, Turnbull's blue, ppt. with $FeSO_4(Fe^{\cdot\cdot})$
Hydroferrocyanic, $H_4Fe(CN)_6$, ferrocyanides	White ppt. Sol. in KCN. Insol. in HNO_3			White ppt. Sol. in HNO_3	Prussian Blue with $FeCl_3$ $(Fe^{\cdot\cdot\cdot})$. Red ppt. with copper salts $(Cu^{\cdot\cdot})$
Hydrofluoric, HF, fluorides		White ppt., BaF_2. Sol. in HCl. 163^{18} mg.	White ppt., CaF_2. Sol. in HCl. Insol. in acetic acid. 1.6 mg.	$Pb(C_2H_3O_2)_2$ ppts. white salt. Sol. in HNO_3	H_2SO_4 evolves HF, which etches glass

Hydrofluosilicic, H_2SiF_6, fluosilicates		White ppt., $BaSiF_6$. Insol. in HCl. $26^{17°}$ mg.			Decomposed by H_2SO_4 into HF and SiF_4. Ppts. K in concentrated solution, as K_2SiF_6, white
Hydrosulfuric, H_2S, sulfides	Black ppt., Ag_2S. Sol. in hot HNO_3. 0.02 mg.			Black ppt., PbS. Sol. in hot HNO_3. 0.1 mg.	Most sulfides decomposed by strong inorganic acids, with odor of rotten eggs (see $AgNO_3$ and $Pb(NO_3)_2$ tests). Colors sodium nitro prussiate, violet
Hypochlorous, HClO, hypochlorites	White ppt., AgClO. Sol. in HNO_3			White ppt., becomes brown on boiling	Cl evolved when salt is treated with HCl and many other acids. Ppts. MnO_2 black from solution of $MnSO_4$
Iodic, HIO_3, iodides	White ppt., $AgIO_3$. Sol. in NH_4OH. Reduced by SO_2 to AgI. 4.4 mg.	White ppt., $Ba(IO_3)_2$. Sol. in HCl. 8 mgs.		White ppt. Sol. in HNO_3	With acetic acid and KI, free iodine formed. CS_2 colored violet. Starch colored blue
Metaphosphoric, HPO_3, metaphosphates	White ppt. Sol. in NH_4OH, HNO_3	White ppt. Sol. in excess of metaphosphate	White ppt. Sol. in dil. acids	White ppt. Sol. in HNO_3	Coagulates albumen. Boiled with $HNO_3 = H_3PO_4$

NORGANIC ACIDS

Acids	$AgNO_3$	$BaCl_2$	$CaCl_2$	$Pb(C_2H_3O_2)_2$	Characteristic Reactions
Nitric, HNO_3, nitrates					H_2SO_4 (conc.) poured into a mixture of a nitrate salt with $FeSO_4$ produces a brown ring at upper surface of heavier H_2SO_4
Nitrous, HNO_2, nitrites	White ppt., $AgNO_2$. Sol. in hot water. 330 mg.				With an iodide, when acidified with HCl, liberates iodine, which will color CS_2 violet
Phosphoric, H_3PO_4, phosphates	Yellow ppt., Ag_3PO_4. Sol. in NH_4OH and HNO_3. 1.93 mg.	White ppt., $Ba_3(PO_4)_2$. Sol. in acids	White ppt. Sol. in inorganic and in acetic acids	White ppt. with Pb salt. Sol. in NaOH. Insol. in NH_4OH. Insol. in $HC_2H_3O_2$. 0.014 mg.	$(NH_4)_2MoO_4+HNO_3$ ppts. at 40°, yellow ammonium phosphomolybdate. Magnesia mixture produces a white ppt., $MgNH_4PO_4$
Phosphorus, H_3PO_3, phosphites	White ppt. On warming, causes reduction of silver salt to Ag	White ppt. Sol. in acids, acetic acid	White ppt. Sol. in NH_4Cl	White ppt. Insol. in $HC_2H_3O_2$. Sol. in HNO_3	Reducing action. Very concentrated solutions heated evolve PH_3
Pyrophosphoric, $H_4P_2O_7$, pyrophosphates	White ppt. Sol. in NH_4OH, HNO_3	White ppt. Sol. in HCl. 10 mg.	White ppt. Sol. in excess of the pyrophosphate	Pb salt same as Ca salt	Does not coagulate albumen as does the metaphosphoric acid. Boiled with HNO_3 changes to H_3PO_4

Silicic, H_2SiO_3, silicates	Yellow ppt. Sol. in HNO_3	White ppt.	White ppt.	White ppt. Insol. in HNO_3	Heated with Na_2CO_3, evolves CO_2. SiO_2 skeleton with $NaPO_3$ bead. Decomposes when evaporated to dryness, SiO_2 separating
Sulfocyanic, HCNS, thiocyanates or sulfo-cyanates	White ppt., AgCNS. Difficultly sol. in NH_4OH. 0.021 mg.			White ppt.	$FeCl_3$ produces a blood-red color, which is destroyed by $HgCl_2$
Sulfuric, H_2SO_4, sulfates	Conc. $AgNO_3$ produces white ppt., Ag_2SO_4. Sol. in water. 580 mg.	White ppt., $BaSO_4$. Insol. in acids. 0.172 mg.	White ppt. Sol. in water and acids	White ppt. Sol. in NaOH, $NH_4C_2H_3O_2$, $(NH_4)_2C_4H_4O_6$	Sulfates heated with Na_2CO_3 on charcoal in reducing flame from Na_2S, which blacken a silver coin when it is moistened
Sulfurous, H_2SO_3, sulfites	White ppt., Ag_2SO_3. Decomposed by boiling into $Ag+Ag_2SO_4+SO_2$	White ppt. Sol. in HCl. 19.7 mg.	White ppt. Sol. in HCl	White ppt.	Reducing agent. Reduces KI (starch sol. test). Decolorizes $KMnO_4 \cdot SO_2$ evolved when salt is acidified with HCl
Thiosulfuric, $H_2S_2O_3$, thiosulfates	$Ag_2S_2O_3$, white ppt. Sol. in $Na_2S_2O_3$. Decomposed by boiling, forming $H_2SO_4+Ag_2S$	Conc. solution produces white ppt.		White ppt. On boiling becomes gray. $PbSO_4+PbS$	Decomposed by HCl to SO_2+S. $Na_2S_2O_3$ dissolves AgCl

ORGANIC ACIDS

Acids	$AgNO_3$	$CaCl_2$	$FeCl_3$	H_2SO_4 Conc.	Special Tests
Acetic, $H \cdot C_2H_3O_2$	White ppt. Sol. in hot water		Reddish brown solution. Ppts. on boiling of ferric acetate = $Fe_2(OH)_2A_4$. Sol. in HCl	Heated, gives odor of vinegar	H_2SO_4+alcohol = ethyl acetate, recognized by characteristic odor
Benzoic, C_6H_5COOH	White ppt. C_6H_5COOAg. Sol. in hot water		Buff-colored ppt. $(CH_5COO)FeOH$. Sol. in HCl	Dissolves without charring or evolution of gas	$Pb(C_2H_3O_2)_2$ ppts. white compound. m.p. 121°, sublimes when heated. $H_2SO_4+C_2H_5OH$ heated = ethyl benzoate
Carbolic, C_6H_5OH			Deep violet. Color destroyed by acetic acid (not destroyed in case of salicylic acid)		Bromine water, even in very dilute solutions, gives a white ppt. sol. in NaOH, KOH. C_6H_5OH+1 ml. $H_2SO_4+NaNO_2$ warmed = deep green or blue color
Citric, C_3H_4OH-$(COOH)_3$	White ppt. Sol. in NH_4OH. No reduction on heating	White ppt. Less sol. in hot than cold water. Sol. in NH_4Cl. Insol. in NaOH. Crystalline form insol. in NH_4Cl			White ppt. with lead acetate. Sol. in ammonium citrate. Prevents pption. of $Fe(OH)_3$ by alkalies. $CdCl_2$ ppts. $Cd(C_6H_5O_7)_2$. Insol. in hot water. Sol. in acetic acid (Cd salts, no ppt. with tartrates)
Formic, HCOOH	White ppt. in conc. solutions. Becomes dark from reduced silver salt		Red ppt. Color destroyed by HCl	With reducing agent heated, gives CO, which burns with blue flame	H_2SO_4 (conc.)+ethyl alcohol = ethyl formate, pleasant characteristic odor

Gallic, $C_6H_2(OH)_3$-COOH	Metallic Ag from reduction		Blue-black ppt. Sol. in excess = green		Melts at 200°. The alkaline solutions absorbs O. Limewater or $Ba(OH)_2$ produces a blue ppt.
Lactic, $C_2H_4OHCOOH$	Reduction results. Ag formed (no action on Fehling's sol.)			Charring on heating with evolution of CO	Decolorizes $KMnO_4$ and effervescence takes place, with odor of acetaldehyde
Malic, C_2H_3OH-$(COOH)_2$	White ppt.	White ppt. only in presence of strong alcohol (distinction from citric)			Lead acetate ppts. white salt. Sol. in hot water. Prevents pption. of $Fe(OH)_3$ by alkalies
Oxalic, $H_2 \cdot C_2O_4$	White ppt. Sol. in HNO_3, NH_4OH	White ppt. Insol. in acetic acid. Sol. in HCl, HNO_3		Heated, CO_2 and CO evolved	H_2SO_4 (dilute) + MnO_2 gives CO_2. Destroys color of $KMnO_4$ when heated with that reagent in presence of dilute H_2SO_4
Salicylic, $C_6H_4OHCOOH$	White ppt. Sol. in hot water, $C_6H_4OHCOOAg$		Deep violet color. Destroyed by mineral acids	Dissolves. Prolonged heating darkens solution and gas is evolved	Lead acetate ppts. a white salt. Acid m.p. 156°. HNO_3 heated with salt produces yellow picric acid. Color is intensified by caustic soda
Tannic, $C_{14}H_{10}O_9$	White ppt.		Blue-black color (ink)		Lead acetate gives a yellow ppt., with astringent taste. The acid ppts. a solution of glue. Limewater produces a gray ppt.
Tartaric, $H_2 \cdot C_4H_4O_6$	White ppt. Sol. in excess of tartrate, HCl, NH_4OH. Reduction on heating	White crystalline ppt. Action similar to magnesium precipitation			Chars when heated. Odor of burnt sugar. Prevents pption. of $Fe(OH)_3$ by alkalies.

SOLUBILITY TABLE

Since no salt is absolutely insoluble, the term "insoluble" is only relative. For solubility of the salts formed, see Van Nostrand's *Chemical Annual*, edited by Professor John C. Olsen.

Anion → / Cation ↓	F'	Cl'	Br'	I'	CN'	NO_3'	ClO_3'	$C_2H_3O_2'$	S''	CO_3''	SiO_3''	SO_4''	CrO_4''	BO_3''', BO_2'	PO_4'''	AsO_4'''	AsO_3'''	$Fe(CN)_6'''$	$Fe(CN)_6''''$	C_2O_4''
$K^{\cdot}$	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
$Na^{\cdot}$	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
$Li^{\cdot}$	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
$Ba^{\cdot\cdot}$	wa	W	W	W	wA	W	W	W	W	A	A	I	A	A	A	A	A	—	wA	—
$Sr^{\cdot\cdot}$	wa	W	W	W	W	W	W	W	W	A	A	I	wA	A	A	A	A	—	W	—
$Ca^{\cdot\cdot}$	wa	W	W	W	W	W	W	W	W	A	A	wa	wA	A	A	A	A	W	W	—
$Mg^{\cdot\cdot}$	wa	W	W	W	W	W	W	wA	W	A	A	W	W	wA	A	A	A	W	W	—
$Al^{\cdot\cdot\cdot}$	W	W	W	W	—	W	W	W	—	—	wa	W	—	A	A	A	—	—	—	—
$Mn^{\cdot\cdot}$	A	W	W	W	A	W	W	wA	A	A	A	W	W	A	A	A	A	I	A	—
$Zn^{\cdot\cdot}$	wA	W	W	W	A	W	W	W	A	A	A	W	W	A	A	A	—	A	wa	—
$Cr^{\cdot\cdot\cdot}$	W	W	W	W	A	W	W	wA	—	—	A	W	A	A	A	A	—	—	—	—
$Cd^{\cdot\cdot}$	wA	W	W	W	A	W	W	W	A	A	A	W	W	wA	A	—	—	—	—	—
$Fe^{\cdot\cdot}$	wA	W	W	W	wa	W	W	W	A	A	A	W	—	A	A	A	A	I	I	—
$Fe^{\cdot\cdot\cdot}$	W	W	W	—	—	W	W	A	—	—	A	W	W	A	A	A	A	W	I	—
$Co^{\cdot\cdot}$	wA	W	W	W	wa	W	W	W	A	A	A	W	A	A	A	A	A	I	I	—
$Ni^{\cdot\cdot}$	wA	W	W	W	wa	W	W	W	A	A	A	W	A	A	A	A	A	I	I	—
$Sn^{\cdot\cdot}$	W	W	—	W	—	W	W	A	A	—	—	W	A	A	A	—	—	I	I	—
$Sn^{\cdot\cdot\cdot\cdot}$	W	W	—	W	—	—	—	—	A	—	—	—	—	—	A	A	A	—	I	—
$Pb^{\cdot\cdot}$	A	W	W	W	A	W	W	W	A	A	A	I	I	A	A	A	—	wA	A	—
$Cu^{\cdot\cdot}$	A	W	W	I	I	W	W	W	A	A	—	W	W	A	A	A	A	—	I	—
$Sb^{\cdot\cdot\cdot}$	W	A	A	wA	—	—	—	A	A	—	—	A	A	—	A	A	—	—	—	—
$Bi^{\cdot\cdot\cdot}$	W	A	A	A	—	A	W	A	A	A	A	A	A	A	A	A	—	—	—	—
$Hg^{\cdot}$	—	I	I	I	—	W	W	A	—	A	—	wA	A	—	A	A	A	—	—	—
$Hg^{\cdot\cdot}$	wA	W	W	A	W	W	W	A	A	A	—	W	wA	—	A	A	A	—		—
$Ag^{\cdot}$	W	I	I	I	I	W	W	A	A	A	A	wA	A	A	A	A	A	A	I	—
$Pt^{\cdot\cdot\cdot\cdot}$	—	W	W	I	W	W	—	—	A	—	—	W	—	—	—	—	A	—	—	—
$Au^{\cdot\cdot\cdot}$	—	W	W	A	W	—	—	—	A	—	—	—	—	—	—	—	—	—	—	—

ABBREVIATIONS.—W = soluble in water; A = soluble in acids; wA = slightly soluble in water, readily soluble in acids; wa = difficultly soluble in water and in acids; I = insoluble in water and acids.

The metals are arranged in order of their electromotive series.

VOL. I

PART III

ACID AND ALKALI TABLES AND OTHER USEFUL DATA

TABLES AND USEFUL DATA

I.—MELTING-POINTS OF THE CHEMICAL ELEMENTS*

Reproduced from Circular No. 35 (2d edition) of U. S. Bureau of Standards

Element	C.	F.
Helium	< −272.2	< −456
Hydrogen	−259	−434
Neon	−248.67	−414.4
Fluorine	−223	−369
Oxygen	−218	−360
Nitrogen	−209.86	−344
Argon	−189.2	−308
Krypton	−169	−272
Xenon	−140	−220
Chlorine	−101.5	−150.7
Mercury	− 38.9	− 38.0
Bromine	− 7.3	+ 18.9
Caesium	+ 26	79
Gallium	30	86
Rubidium	38.5	100
Phosphorus	44	111.2
Potassium	62.3	144
Sodium	97.5	207.5
Iodine	113.5	236.3
	S_I 112.8	235.0
Sulfur	S_{II} 119.2	246.6
	S_{III} 106.8	224.2
Indium	155	311
Lithium	186	367
Selenium	217–220	422–428
TIN	231.9	449.4
Bismuth	271	520
Thallium	303.5	577
CADMIUM	320.9	609.6
LEAD	327.4	621.3
ZINC	419.4	786.9
Tellurium	452	846
ANTIMONY	630.0	1166
Cerium	640	1184
Magnesium	651	1204
ALUMINUM	660	1220
Radium	960	1760
Calcium	810	1490
Lanthanum	826	1518.8
Strontium	800	

Element	C.	F.
Neodymium	840	1544
Arsenic	814	1497
Barium	850	1562
Praseodymium	940	1724
Germanium	958	1756
SILVER	960.5	1761
GOLD	1063.0	1945.5
COPPER	1083.0	1981.5
Manganese	1260	2300
Samarium	1300–1400	2370–2550
Beryllium (glucinum)	1350	2462
Scandium	1200	2192
Silicon	1420	2588
NICKEL	1452	2646
Cobalt	1480	2696
Yttrium	1490	2714
Chromium	1615	2768
IRON	1535	2795
PALLADIUM	1555	2831
Zirconium	1700	3090
Columbium (Niobium)	1950	3542
Thorium	1845	3353
Vanadium	1710	3110
PLATINUM	1755	3191
Ytterbium	1490	2714
Titanium	1800	3272
Uranium	<1850	<3362
Rhodium	1955	3551
Boron	2300	4172
Iridium	2350	4262
Ruthenium	2450	4442
Molybdenum	2620±10	4748
Osmium	2700	4900
Tantalum	2850	5160
TUNGSTEN	3370	6066
Carbon	>3500 for p. = 1 at.	>6300 for p. = 1 at.

II.—OTHER TEMPERATURE STANDARDS

Temperatures of Flames †

	Cent.	Deg. of Accuracy
Bunsen, open	1100	Within 100° C.‡
Meker	1500*	
Petrol blow lamp	1600*	
Oxyhydrogen with H_2+O	2420	Within 100° C.
Oxyacetylene	2400*	
Thermit	2500	
Electric arc	3500	Within 150° C.
Sun	6000	Within 500° C.

* Chemical and Metallurgical Engineering, Vol. XIII, No. 5, May, 1915.

† Measurement of High Temperatures, G. K. Burgess and H. Le Chatelier.

‡ Pyrometer tests of the open Bunsen flame gave temperatures ranging from 1000° to 1100° C.

III.—OTHER TEMPERATURE STANDARDS

Approximate Temperatures by Colors

	Cent.	Fahr.
First visible red	525	977
Dull red	700	1292
Cherry red	900	1652
Dull orange	1100	2012
White	1300	2372
Dazzling white	1500	2732

Substance	Phenomenon	C.	F.	Variation with Pressure (pressure in mm. of Hg)
Oxygen	Boiling	−183.0	−297.4	C. ° = −183.0+0.01258 (p-760) −0.0000079 (p-760)
Carbon dioxide	Sublimation in inert liquid	− 78.5	−109.3	C. ° = −78.5+0.017 (p-760)
Sodium sulfate, $Na_2SO_4+10H_2O$	Transformation into anhydrous salt	32.384	90.291	
Water	Boiling	100	212	C. ° = −100+0.03670 (p-760) −0.00002046 (p-760)
Naphthalene	Boiling	240.2	460.7	C. ° = 217.96+0.058 (p-760)
Benzophenone	Boiling	305.9	582.6	C. ° = 305.9+0.063 (p-760)
Sulfur	Boiling	444.6	832.3	C. ° = 444.6+0.0908 (p-760) −0.000047 (p-760)
Ag_3Cu_2	Eutectic Freezing	779	1434	
Sodium chloride	Freezing	801	1472	

IV.—ELECTROMOTIVE ARRANGEMENT OF THE ELEMENTS*

Each metallic element is positive to the element placed after it. The order, however, depends upon certain factors, temperature, electrolyte, etc. For example, Zn precipitates Cu from $CuSO_4$, Fe from $FeSO_4$, but Cu and Fe precipitate Zn from KCN solution. Pt liberates H from H_2O containing KCN.

Metals			Negative Elements
1. Li	11. Mn	23. As	Si
2. Na	12. Zn	24. Cu	C
3. K	13. Cr	25. Hg	B
4. Rb	14. Cd	26. Ag	N
5. Cs	15. Fe	27. Pd	Se
6. Ca	16. Co	28. Pt	P
7. Sr	17. Ni	29. Au	S
8. Ba	18. Sn	30. Ir	I
9. Mg	19. Pb	31. Rh	Br
10. Al	20. H	32. Os	Cl
	21. Sb		O
	22. Bi		F

* J. W. Mellor.

ACID AND ALKALI TABLES

V.—HYDROCHLORIC ACID

By W. C. Ferguson

Degrees Baumé.	Sp. Gr.	Degrees Twaddell.	Per Cent HCl.	Degrees Baumé.	Sp. Gr.	Degrees Twaddell.	Per Cent HCl.
1.00	1.0069	1.38	1.40	14.25	1.1090	21.80	21.68
2.00	1.0140	2.80	2.82	14.50	1.1111	22.22	22.09
3.00	1.0211	4.22	4.25	14.75	1.1132	22.64	22.50
4.00	1.0284	5.68	5.69	15.00	1.1154	23.08	22.92
5.00	1.0357	7.14	7.15	15.25	1.1176	23.52	23.33
5.25	1.0375	7.50	7.52	15.50	1.1197	23.94	23.75
5.50	1.0394	7.88	7.89	15.75	1.1219	24.38	24.16
5.75	1.0413	8.26	8.26	16.0	1.1240	24.80	24.57
6.00	1.0432	8.64	8.64	16.1	1.1248	24.96	24.73
6.25	1.0450	9.00	9.02	16.2	1.1256	25.12	24.90
6.50	1.0469	9.38	9.40	16.3	1.1265	25.30	25.06
6.75	1.0488	9.76	9.78	16.4	1.1274	25.48	25.23
7.00	1.0507	10.14	10.17	16.5	1.1283	25.66	25.39
7.25	1.0526	10.52	10.55	16.6	1.1292	25.84	25.56
7.50	1.0545	10.90	10.94	16.7	1.1301	26.02	25.72
7.75	1.0564	11.28	11.32	16.8	1.1310	26.20	25.89
8.00	1.0584	11.68	11.71	16.9	1.1319	26.38	26.05
8.25	1.0603	12.06	12.09	17.0	1.1328	26.56	26.22
8.50	1.0623	12.46	12.48	17.1	1.1336	26.72	26.39
8.75	1.0642	12.84	12.87	17.2	1.1345	26.90	26.56
9.00	1.0662	13.24	13.26	17.3	1.1354	27.08	26.73
9.25	1.0681	13.62	13.65	17.4	1.1363	27.26	26.90
9.50	1.0701	14.02	14.04	17.5	1.1372	27.44	27.07
9.75	1.0721	14.42	14.43	17.6	1.1381	27.62	27.24
10.00	1.0741	14.82	14.83	17.7	1.1390	27.80	27.41
10.25	1.0761	15.22	15.22	17.8	1.1399	27.98	27.58
10.50	1.0781	15.62	15.62	17.9	1.1408	28.16	27.75
10.75	1.0801	16.02	16.01	18.0	1.1417	28.34	27.92
11.00	1.0821	16.42	16.41	18.1	1.1426	28.52	28.09
11.25	1.0841	16.82	16.81	18.2	1.1435	28.70	28.26
11.50	1.0861	17.22	17.21	18.3	1.1444	28.88	28.44
11.75	1.0881	17.62	17.61	18.4	1.1453	29.06	28.61
12.00	1.0902	18.04	18.01	18.5	1.1462	29.24	28.78
12.25	1.0922	18.44	18.41	18.6	1.1471	29.42	28.95
12.50	1.0943	18.86	18.82	18.7	1.1480	29.60	29.13
12.75	1.0964	19.28	19.22	18.8	1.1489	29.78	29.30
13.00	1.0985	19.70	19.63	18.9	1.1498	29.96	29.48
13.25	1.1006	20.12	20.04	19.0	1.1508	30.16	29.65
13.50	1.1027	20.54	20.45	19.1	1.1517	30.34	29.83
13.75	1.1048	20.96	20.86	19.2	1.1526	30.52	30.00
14.00	1.1069	21.38	21.27	19.3	1.1535	30.70	30.18

V.—HYDROCHLORIC ACID (Continued)

Degrees Baumé.	Sp. Gr.	Degrees Twaddell.	Per Cent HCl.	Degrees Baumé.	Sp. Gr.	Degrees Twaddell.	Per Cent HCl.
19.4	1.1544	30.88	30.35	22.5	1.1836	36.72	36.16
19.5	1.1554	31.08	30.53	22.6	1.1846	36.92	36.35
19.6	1.1563	31.26	30.71	22.7	1.1856	37.12	36.54
19.7	1.1572	31.44	30.90	22.8	1.1866	37.32	36.73
19.8	1.1581	31.62	31.08	22.9	1.1875	37.50	36.93
19.9	1.1590	31.80	31.27	23.0	1.1885	37.70	37.14
20.0	1.1600	32.00	31.45	23.1	1 1895	37.90	37.36
20.1	1.1609	32.18	31.64	23.2	1.1904	38.08	37.58
20.2	1.1619	32.38	31.82	23.3	1.1914	38.28	37.80
20.3	1.1628	32.56	32.01	23.4	1.1924	38.48	38.03
20.4	1.1637	32.74	32.19	23.5	1.1934	38.68	38.26
20.5	1.1647	32.94	32.38	23.6	1.1944	38.88	38.49
20.6	1.1656	33.12	32.56	23.7	1.1953	39.06	38.72
20.7	1.1666	33.32	32.75	23.8	1.1963	39.26	38.95
20.8	1.1675	33.50	32.93	23.9	1.1973	39.46	39.18
20.9	1.1684	33.68	33.12	24.0	1.1983	39.66	39.41
21.0	1.1694	33.88	33.31	24.1	1.1993	39.86	39.64
21.1	1.1703	34.06	33.50	24.2	1.2003	40.06	39.86
21.2	1.1713	34.26	33.69	24.3	1.2013	40.26	40.09
21.3	1.1722	34.44	33.88	24.4	1.2023	40.46	40.32
21.4	1.1732	34.64	34.07	24.5	1.2033	40.66	40.55
21 5	1.1741	34.82	34.26	24.6	1.2043	40.86	40.78
21.6	1.1751	35.02	34.45	24.7	1.2053	41.06	41.01
21.7	1.1760	35.20	34.64	24.8	1.2063	41.26	41.24
21.8	1.1770	35.40	34.83	24.9	1.2073	41.46	41.48
21.9	1.1779	35.58	35.02	25.0	1.2083	41.66	41.72
22.0	1.1789	35.78	35.21	25.1	1.2093	41.86	41.99
22.1	1.1798	35.96	35.40	25.2	1.2103	42.06	42.30
22.2	1.1808	36.16	35.59	25.3	1.2114	42.28	42.64
22.3	1.1817	36.34	35.78	25.4	1.2124	42.48	43.01
22.4	1.1827	36.54	35.97	25.5	1.2134	42.68	43.40

Sp. Gr. determinations were made at 60° F., compared with water at 60° F. From the Specific Gravities, the corresponding degrees Baumé were calculated by the following formula: Baumé = 145 – 145/Sp. Gr.

Atomic weights from F. W. Clarke's table of 1901. O = 16.

ALLOWANCE FOR TEMPERATURE:

10–15° Bé. – 1/40° Bé. or .0002 Sp. Gr. for 1° F.
15–22° Bé. – 1/30° Bé. or .0003 " " " 1° F.
22–25° Bé. – 1/28° Bé. or .00035 " " " 1° F.

AUTHORITY — W. C. FERGUSON.

This table has been approved and adopted as a Standard by the Manufacturing Chemists' Association of the United States.

W. H. BOWER, JAS. L. MORGAN,
HENRY HOWARD, ARTHUR WYMAN,
A. G. ROSENGARTEN,
Executive Committee.

New York, May 14, 1903.

VI.—HYDROCHLORIC ACID

Lunge and Marchlewski

Specific Gravity $\frac{15^\circ}{4^\circ}$ in Vacuo.	Per Cent HCl by Weight.	1 Liter contains Grams HCl.	Specific Gravity $\frac{15^\circ}{4^\circ}$ in Vacuo.	Per Cent HCl by Weight.	1 Liter contains Grams HCl.	Specific Gravity $\frac{15^\circ}{4^\circ}$ in Vacuo.	Per Cent HCl by Weight.	1 Liter contains Grams HCl.
1.000	0.16	1.6	1.075	15.16	163	1.145	28.61	328
1.005	1.15	12	1.080	16.15	174	1.150	29.57	340
1.010	2.14	22	1.085	17.13	186	1.152	29.95	345
1.015	3.12	32	1.090	18.11	197	1.155	30.55	353
1.020	4.13	42	1.095	19.06	209	1.160	31.52	366
1.025	5.15	53	1.100	20.01	220	1.163	32.10	373
1.030	6.15	64	1.105	20.97	232	1.165	32.49	379
1.035	7.15	74	1.110	21.92	243	1.170	33.46	392
1.040	8.16	85	1.115	22.86	255	1.171	33.65	394
1.045	9.16	96	1.120	23.82	267	1.175	34.42	404
1.050	10.17	107	1.125	24.78	278	1.180	35.39	418
1.055	11.18	118	1.130	25.75	291	1.185	36.31	430
1.060	12.19	129	1.135	26.70	303	1.190	37.23	443
1.065	13.19	141	1.140	27.66	315	1.195	38.16	456
1.070	14.17	152	1.1425	28.14	322	1.200	39.11	469

COMPOSITION OF CONSTANT BOILING HYDROCHLORIC ACID*

Pressure mm. of Mercury	Per Cent of HCl.	Grams constant boiling distillate for 1 mol. HCl.	Barometer mm.	Per Cent of HCl.	Grams of acid weighed in air for 1 liter of N acid †
770	20.218	180.390	770	20.197	180.407
760	20.242	180.170	760	20.221	180.193
750	20.266	179.960	750	20.245	179.979
740	20.290	179.745	740	20.269	179.766
730	20.314	179.530	730	20.293	179.555

Temperature of constant boiling hydrochloric acid is 108.54° at 763 mm. Specific gravity 1.09620[25].

* Hulett and Bonner, J. Am. Chem. Soc., 31, 390 (1909).

† Data of Foulk and Hollingsworth, J. Am. Chem. Soc. 45, 1220 (1923).

VII.—NITRIC ACID

By W. C. Ferguson

Degrees Baumé.	Sp. Gr. $\frac{60°}{60°}$ F.	Degrees Twaddell.	Per Cent HNO_3.	Degrees Baumé.	Sp. Gr. $\frac{60°}{60°}$ F.	Degrees Twaddell.	Per Cent HNO_3.
10.00	1.0741	14.82	12.86	21.25	1.1718	34.36	28.02
10.25	1.0761	15.22	13.18	21.50	1.1741	34.82	28.36
10.50	1.0781	15.62	13.49	21.75	1.1765	35.30	28.72
10.75	1.0801	16.02	13.81	22.00	1.1789	35.78	29.07
11.00	1.0821	16.42	14.13	22.25	1.1813	36.26	29.43
11.25	1.0841	16.82	14.44	22.50	1.1837	36.74	29.78
11.50	1.0861	17.22	14.76	22.75	1.1861	37.22	30.14
11.75	1.0881	17.62	15.07	23.00	1.1885	37.70	30.49
12.00	1.0902	18.04	15.41	23.25	1.1910	38.20	30.86
12.25	1.0922	18.44	15.72	23.50	1.1934	38.68	31.21
12.50	1.0943	18.86	16.05	23.75	1.1959	39.18	31.58
12.75	1.0964	19.28	16.39	24.00	1.1983	39.66	31.94
13.00	1.0985	19.70	16.72	24.25	1.2008	40.16	32.31
13.25	1.1006	20.12	17.05	24.50	1.2033	40.66	32.68
13.50	1.1027	20.54	17.38	24.75	1.2058	41.16	33.05
13.75	1.1048	20.96	17.71	25.00	1.2083	41.66	33.42
14.00	1.1069	21.38	18.04	25.25	1.2109	42.18	33.80
14.25	1.1090	21.80	18.37	25.50	1.2134	42.68	34.17
14.50	1.1111	22.22	18.70	25.75	1.2160	43.20	34.56
14.75	1.1132	22.64	19.02	26.00	1.2185	43.70	34.94
15.00	1.1154	23.08	19.36	26.25	1.2211	44.22	35.33
15.25	1.1176	23.52	19.70	26.50	1.2236	44.72	35.70
15.50	1.1197	23.94	20.02	26.75	1.2262	45.24	36.09
15.75	1.1219	24.38	20.36	27.00	1.2288	45.76	36.48
16.00	1.1240	24.80	20.69	27.25	1.2314	46.28	36.87
16.25	1.1262	25.24	21.03	27.50	1.2340	46.80	37.26
16.50	1.1284	25.68	21.36	27.75	1.2367	47.34	37.67
16.75	1.1306	26.12	21.70	28.00	1.2393	47.86	38.06
17.00	1.1328	26.56	22.04	28.25	1.2420	48.40	38.46
17.25	1.1350	27.00	22.38	28.50	1.2446	48.92	38.85
17.50	1.1373	27.46	22.74	28.75	1.2473	49.46	39.25
17.75	1.1395	27.90	23.08	29.00	1.2500	50.00	39.66
18.00	1.1417	28.34	23.42	29.25	1.2527	50.54	40.06
18.25	1.1440	28.80	23.77	29.50	1.2554	51.08	40.47
18.50	1.1462	29.24	24.11	29.75	1.2582	51.64	40.89
18.75	1.1485	29.70	24.47	30.00	1.2609	52.18	41.30
19.00	1.1508	30.16	24.82	30.25	1.2637	52.74	41.72
19.25	1.1531	30.62	25.18	30.50	1.2664	53.28	42.14
19.50	1.1554	31.08	25.53	30.75	1.2692	53.84	42.58
19.75	1.1577	31.54	25.88	31.00	1.2719	54.38	43.00
20.00	1.1600	32.00	26.24	31.25	1.2747	54.94	43.44
20.25	1.1624	32.48	26.61	31.50	1.2775	55.50	43.89
20.50	1.1647	32.94	26.96	31.75	1.2804	56.08	44.34
20.75	1.1671	33.42	27.33	32.00	1.2832	56.64	44.78
21.00	1.1694	33.88	27.67	32.25	1.2861	57.22	45.24

VII.—NITRIC ACID (Continued)

Degrees Baumé.	Sp. Gr. $\frac{60°}{60°}$ F.	Degrees Twaddell.	Per Cent HNO_3.	Degrees Baumé.	Sp. Gr. $\frac{60°}{60°}$ F.	Degrees Twaddell.	Per Cent HNO_3.
32.50	1.2889	57.78	45.68	40.75	1.3909	78.18	63.48
32.75	1.2918	58.36	46.14	41.00	1.3942	78.84	64.20
33.00	1.2946	58.92	46.58	41.25	1.3976	79.52	64.93
33.25	1.2975	59.50	47.04	41.50	1.4010	80.20	65.67
33.50	1.3004	60.08	47.49	41.75	1.4044	80.88	66.42
33.75	1.3034	60.68	47.95	42.00	1.4078	81.56	67.18
34.00	1.3063	61.26	48.42	42.25	1.4112	82.24	67.95
34.25	1.3093	61.86	48.90	42.50	1.4146	82.92	68.73
34.50	1.3122	62.44	49.35	42.75	1.4181	83.62	69.52
34.75	1.3152	63.04	49.83	43.00	1.4216	84.32	70.33
35.00	1.3182	63.64	50.32	43.25	1.4251	85.02	71.15
35.25	1.3212	64.24	50.81	43.50	1.4286	85.72	71.98
35.50	1.3242	64.84	51.30	43.75	1.4321	86.42	72.82
35.75	1.3273	65.46	51.80	44.00	1.4356	87.12	73.67
36.00	1.3303	66.06	52.30	44.25	1.4392	87.84	74.53
36.25	1.3334	66.68	52.81	44.50	1.4428	88.56	75.40
36.50	1.3364	67.28	53.32	44.75	1.4464	89.28	76.28
36.75	1.3395	67.90	53.84	45.00	1.4500	90.00	77.17
37.00	1.3426	68.52	54.36	45.25	1.4536	90.72	78.07
37.25	1.3457	69.14	54.89	45.50	1.4573	91.46	79.03
37.50	1.3488	69.76	55.43	45.75	1.4610	92.20	80.04
37.75	1.3520	70.40	55.97	46.00	1.4646	92.92	81.08
38.00	1.3551	71.02	56.52	46.25	1.4684	93.68	82.18
38.25	1.3583	71.66	57.08	46.50	1.4721	94.42	83.33
38.50	1.3615	72.30	57.65	46.75	1.4758	95.16	84.48
38.75	1.3647	72.94	58.23	47.00	1.4796	95.92	85.70
39.00	1.3679	73.58	58.82	47.25	1.4834	96.68	86.98
39.25	1.3712	74.24	59.43	47.50	1.4872	97.44	88.32
39.50	1.3744	74.88	60.06	47.75	1.4910	98.20	89.76
39.75	1.3777	75.54	60.71	48.00	1.4948	98.96	91.35
40.00	1.3810	76.20	61.38	48.25	1.4987	99.74	93.13
40.25	1.3843	76.86	62.07	48.50	1.5026	100.52	95.11
40.50	1.3876	77.52	62.77				

Specific Gravity determinations were made at 60° F., compared with water at 60° F.

From the Specific Gravities, the corresponding degrees Baumé were calculated by the following formula:

$$\text{Baumé} = 145 - \frac{145}{\text{Sp. Gr.}}.$$

Baumé Hydrometers for use with this table must be graduated by the above formula, which formula should always be printed on the scale.

Atomic weights from F. W. Clarke's table of 1901. O = 16.

ALLOWANCE FOR TEMPERATURE:

At 10° — 20° Bé. — 1/30° Bé. or .00029 Sp. Gr. = 1° F.
20° — 30° Bé. — 1/23° Bé. or .00044 " " = 1° F.
30° — 40° Bé. — 1/20° Bé. or .00060 " " = 1° F.
40° — 48.5° Bé. — 1/17° Bé. or .00084 " " = 1° F.

AUTHORITY — W. C. FERGUSON.

This table has been approved and adopted as a Standard by the Manufacturing Chemists' Association of the United States.

W. H. BOWER, JAS. L. MORGAN,
HENRY HOWARD, ARTHUR WYMAN,
A. G. ROSENGARTEN, *Executive Committee*

New York, May 14, 1903.

VIII.—NITRIC ACID

LUNGE AND REY

Specific Gravity $\frac{15^\circ}{4^\circ}$ in vacuo	100 parts by weight contain		1 liter contains grams		Specific Gravity $\frac{15^\circ}{4^\circ}$ in vacuo	100 parts by weight contain		1 liter contains grams	
	% N_2O_5	% HNO_3	N_2O_5	HNO_3		% N_2O_5	% HNO_3	N_2O_5	HNO_3
1.000	0.08	0.10	1	1	1.195	27.10	31.62	324	378
1.005	0.85	1.00	8	10	1.200	27.74	32.36	333	388
1.010	1.62	1.90	16	19	1.205	28.36	33.09	342	399
1.015	2.39	2.80	24	28	1.210	28.99	33.82	351	409
1.020	3.17	3.70	33	38	1.215	29.61	34.55	360	420
1.025	3.94	4.60	40	47	1.220	30.24	35.28	369	430
1.030	4.71	5.50	49	57	1.225	30.88	36.03	378	441
1.035	5.47	6.38	57	66	1.230	31.53	36.78	387	452
1.040	6.22	7.26	64	75	1.235	32.17	37.53	397	463
1.045	6.97	8.13	73	85	1.240	32.82	38.29	407	475
1.050	7.71	8.99	81	94	1.245	33.47	39.05	417	486
1.055	8.43	9.84	89	104	1.250	34.13	39.82	427	498
1.060	9.15	10.68	97	113	1.255	34.78	40.58	437	509
1.065	9.87	11.51	105	123	1.260	35.44	41.34	447	521
1.070	10.57	12.33	113	132	1.265	36.09	42.10	457	533
1.075	11.27	13.15	121	141	1.270	36.75	42.87	467	544
1.080	11.96	13.95	129	151	1.275	37.41	43.64	477	556
1.085	12.64	14.74	137	160	1.280	38.07	44.41	487	568
1.090	13.31	15.53	145	169	1.285	38.73	45.18	498	581
1.095	13.99	16.32	153	179	1.290	39.39	45.95	508	593
1.100	14.67	17.11	161	188	1.295	40.05	46.72	519	605
1.105	15.34	17.89	170	198	1.300	40.71	47.49	529	617
1.110	16.00	18.67	177	207	1.305	41.37	48.26	540	630
1.115	16.67	19.45	186	217	1.310	42.06	49.07	551	643
1.120	17.34	20.23	195	227	1.315	42.76	49.89	562	656
1.125	18.00	21.00	202	236	1.320	43.47	50.71	573	669
1.130	18.66	21.77	211	246	1.325	44.17	51.53	585	683
1.135	19.32	22.54	219	256	1.330	44.89	52.37	597	697
1.140	19.98	23.31	228	266	1.3325	45.26	52.80	603	704
1.145	20.64	24.08	237	276	1.335	45.62	53.22	609	710
1.150	21.29	24.84	245	286	1.340	46.35	54.07	621	725
1.155	21.94	25.60	254	296	1.345	47.08	54.93	633	739
1.160	22.60	26.36	262	306	1.350	47.82	55.79	645	753
1.165	23.25	27.12	271	316	1.355	48.57	56.66	658	768
1.170	23.90	27.88	279	326	1.360	49.35	57.57	671	783
1.175	24.54	28.63	288	336	1.365	50.13	58.48	684	798
1.180	25.18	29.38	297	347	1.370	50.91	59.39	698	814
1.185	25.83	30.13	306	357	1.375	51.69	60.30	711	829
1.190	26.47	30.88	315	367	1.380	52.52	61.27	725	846

VIII.—NITRIC ACID (Continued)

Specific Gravity $\frac{15^\circ}{4^\circ}$ in vacuo	100 parts by weight contain		1 liter contains grams		Specific Gravity $\frac{15^\circ}{4^\circ}$ in vacuo	100 parts by weight contain		1 liter contains grams	
	% N_2O_5	% HNO_3	N_2O_5	HNO_3		% N_2O_5	% HNO_3	N_2O_5	HNO_3
1.3833	53.08	61.92	735	857	1.495	78.52	91.60	1174	1369
1.385	53.35	62.24	739	862	1.500	80.65	94.09	1210	1411
1.390	54.20	63.23	753	879	1.501	81.09	94.60	1217	1420
1.395	55.07	64.25	768	896	1.502	81.50	95.08	1224	1428
1.400	55.97	65.30	783	914	1.503	81.91	95.55	1231	1436
1.405	56.92	66.40	800	933	1.504	82.29	96.00	1238	1444
1.410	57.86	67.50	816	952	1.505	82.63	96.39	1244	1451
1.415	58.83	68.63	832	971	1.506	82.94	96.76	1249	1457
1.420	59.83	69.80	849	991	1.507	83.26	97.13	1255	1464
1.425	60.84	70.98	867	1011	1.508	83.58	97.50	1260	1470
1.430	61.86	72.17	885	1032	1.509	83.87	97.84	1265	1476
1.435	62.91	73.39	903	1053	1.510	84.09	98.10	1270	1481
1.440	64.01	74.68	921	1075	1.511	84.28	98.32	1274	1486
1.445	65.13	75.98	941	1098	1.512	84.46	98.53	1277	1490
1.450	66.24	77.28	961	1121	1.513	84.63	98.73	1280	1494
1.455	67.38	78.60	981	1144	1.514	84.78	98.90	1283	1497
1.460	68.56	79.98	1001	1168	1.515	84.92	99.07	1287	1501
1.465	69.79	81.42	1023	1193	1.516	85.04	99.21	1289	1504
1.470	71.06	82.90	1045	1219	1.517	85.15	99.34	1292	1507
1.475	72.39	84.45	1068	1246	1.518	85.26	99.46	1294	1510
1.480	73.76	86.05	1092	1274	1.519	85.35	99.57	1296	1512
1.485	75.18	87.70	1116	1302	1.520	85.44	99.67	1299	1515
1.490	76.80	89.60	1144	1335					

IX.—PHOSPHORIC ACID AT 17.5°

Specific Gravity.	Per Cent. P_2O_5.	Per Cent. H_3PO_4.	Specific Gravity.	Per Cent. P_2O_5.	Per Cent. H_3PO_4.	Specific Gravity.	Per Cent. P_2O_5.	Per Cent. H_3PO_4.
1.809	68.0	93.67	1.462	46.0	63.37	1.208	24.0	33.06
1.800	67.5	92.99	1.455	45.5	62.68	1.203	23.5	32.37
1.792	67.0	92.30	1.448	45.0	61.99	1.198	23.0	31.68
1.783	66.5	91.61	1.441	44.5	61.30	1.193	22.5	30.99
1.775	66.0	90.92	1.435	44.0	60.61	1.188	22.0	30.31
1.766	65.5	90.23	1.428	43.5	59.92	1.183	21.5	29.62
1.758	65.0	89.54	1.422	43.0	59.23	1.178	21.0	28.93
1.750	64.5	88.85	1.415	42.5	58.55	1.174	20.5	28.24
1.741	64.0	88.16	1.409	42.0	57.86	1.169	20.0	27.55
1.733	63.5	87.48	1.402	41.5	57.17	1.164	19.5	26.86
1.725	63.0	86.79	1.396	41.0	56.48	1.159	19.0	26.17
1.717	62.5	86.10	1.389	40.5	55.79	1.155	18.5	25.48
1.709	62.0	85.41	1.383	40.0	55.10	1.150	18.0	24.80
1.701	61.5	84.72	1.377	39.5	54.41	1.145	17.5	24.11
1.693	61.0	84.03	1.371	39.0	53.72	1.140	17.0	23.42
1.685	60.5	83.34	1.365	38.5	53.04	1.135	16.5	22.73
1.677	60.0	82.65	1.359	38.0	52.35	1.130	16.0	22.04
1.669	59.5	81.97	1.354	37.5	51.66	1.126	15.5	21.35
1.661	59.0	81.28	1.348	37.0	50.97	1.122	15.0	20.66
1.653	58.5	80.59	1.342	36.5	50.28	1.118	14.5	19.97
1.645	58.0	79.90	1.336	36.0	49.59	1.113	14.0	19.28
1.637	57.5	79.21	1.330	35.5	48.90	1.109	13.5	18.60
1.629	57.0	78.52	1.325	35.0	48.21	1.104	13.0	17.91
1.621	56.5	77.83	1.319	34.5	47.52	1.100	12.5	17.22
1.613	56.0	77.14	1.314	34.0	46.84	1.096	12.0	16.53
1.605	55.5	76.45	1.308	33.5	46.15	1.091	11.5	15.84
1.597	55.0	75.77	1.303	33.0	45.46	1.087	11.0	15.15
1.589	54.5	75.08	1.298	32.5	44.77	1.083	10.5	14.46
1.581	54.0	74.39	1.292	32.0	44.08	1.079	10.0	13.77
1.574	53.5	73.70	1.287	31.5	43.39	1.074	9.5	13.09
1.566	53.0	73.01	1.281	31.0	42.70	1.070	9.0	12.40
1.559	52.5	72.32	1.276	30.5	42.01	1.066	8.5	11.71
1.551	52.0	71.63	1.271	30.0	41.33	1.062	8.0	11.02
1.543	51.5	70.94	1.265	29.5	40.64	1.058	7.5	10.33
1.536	51.0	70.26	1.260	29.0	39.95	1.053	7.0	9.64
1.528	50.5	69.57	1.255	28.5	39.26	1.049	6.5	8.95
1.521	50.0	68.88	1.249	28.0	38.57	1.045	6.0	8.26
1.513	49.5	68.19	1.244	27.5	37.88	1.041	5.5	7.57
1.505	49.0	67.50	1.239	27.0	37.19	1.037	5.0	6.89
1.498	48.5	66.81	1.233	26.5	36.50	1.033	4.5	6.20
1.491	48.0	66.12	1.228	26.0	35.82	1.029	4.0	5.51
1.484	47.5	65.43	1.223	25.5	35.13	1.025	3.5	4.82
1.476	47.0	64.75	1.218	25.0	34.44	1.021	3.0	4.13
1.469	46.5	64.06	1.213	24.5	33.75	1.017	2.5	3.44

X.—SULFURIC ACID

By W. C. Ferguson and H. P. Talbot

Degrees Baumé.	Specific Gravity $\frac{60°}{60°}$ F.	Degrees Twaddell.	Per Cent H_2SO_4.	Weight of 1 Cu. Ft. in Lbs. Av.	Per Cent O. V.*	Pounds O. V. in 1 Cubic Foot.
0	1.0000	0.0	0.00	62.37	0.00	0.00
1	1.0069	1.4	1.02	62.80	1.09	0.68
2	1.0140	2.8	2.08	63.24	2.23	1.41
3	1.0211	4.2	3.13	63.69	3.36	2.14
4	1.0284	5.7	4.21	64.14	4.52	2.90
5	1.0357	7.1	5.28	64.60	5.67	3.66
6	1.0432	8.6	6.37	65.06	6.84	4.45
7	1.0507	10.1	7.45	65.53	7.99	5.24
8	1.0584	11.7	8.55	66.01	9.17	6.06
9	1.0662	13.2	9.66	66.50	10.37	6.89
10	1.0741	14.8	10.77	66.99	11.56	7.74
11	1.0821	16.4	11.89	67.49	12.76	8.61
12	1.0902	18.0	13.01	68.00	13.96	9.49
13	1.0985	19.7	14.13	68.51	15.16	10.39
14	1.1069	21.4	15.25	69.04	16.36	11.30
15	1.1154	23.1	16.38	69.57	17.58	12.23
16	1.1240	24.8	17.53	70.10	18.81	13.19
17	1.1328	26.6	18.71	70.65	20.08	14.18
18	1.1417	28.3	19.89	71.21	21.34	15.20
19	1.1508	30.2	21.07	71.78	22.61	16.23
20	1.1600	32.0	22.25	72.35	23.87	17.27
21	1.1694	33.9	23.43	72.94	25.14	18.34
22	1.1789	35.8	24.61	73.53	26.41	19.42
23	1.1885	37.7	25.81	74.13	27.69	20.53
24	1.1983	39.7	27.03	74.74	29.00	21.68

Sp. Gr. determinations were made at 60° F., compared with water at 60° F.

From the Sp. Grs., the corresponding degrees Baumé were calculated by the following formula: Baumé = 145 − 145/Sp. Gr.

Baumé Hydrometers for use with this table must be graduated by the above formula, which formula should always be printed on the scale.

* 66° Baumé = Sp. Gr. 1.8354 = Oil of Vitriol (O. V.).
1 cu. ft. water at 60° F. weighs 62.37 lbs. av.
Atomic weights from F. W. Clarke's table of 1901. O = 16.
H_2SO_4 = 100 per cent.

	% H_2SO_4		% O. V.		%60°
O. V.	= 93.19	=	100.00	=	119.98
60°	= 77.67	=	83.35	=	100.00
50°	= 62.18	=	66.72	=	80.06

X.—SULFURIC ACID (Continued)

Degrees Baumé.	* Freezing (Melting) Point. F.
0	32.0
1	31.2
2	30.5
3	29.8
4	28.9
5	28.1
6	27.2
7	26.3
8	25.1
9	24.0
10	22.8
11	21.5
12	20.0
13	18.3
14	16.6
15	14.7
16	12.6
17	10.2
18	7.7
19	4.8
20	+ 1.6
21	− 1.8
22	− 6.0
23	−11
24	−16

APPROXIMATE BOILING POINTS

50° B,	295° F.
60° "	386° "
61° "	400° "
62° "	415° "
63° "	432° "
64° "	451° "
65° "	485° "
66° "	538° "

FIXED POINTS

Specific Gravity.	Per Cent H_2SO_4.	Specific Gravity.	Per Cent H_2SO_4.
1.0000	.00	1.5281	62.34
1.0048	.71	1.5440	63.79
1.0347	5.14	1.5748	66.51
1.0649	9.48	1.6272	71.00
1.0992	14.22	1.6679	74.46
1.1353	19.04	1.7044	77.54
1.1736	23.94	1.7258	79.40
1.2105	28.55	1.7472	81.32
1.2513	33.49	1.7700	83.47
1.2951	38.64	1.7959	86.36
1.3441	44.15	1.8117	88.53
1.3947	49.52	1.8194	89.75
1.4307	53.17	1.8275	91.32
1.4667	56.68	1.8354	93.19
1.4822	58.14		

Acids stronger than 66° Bé. should have their percentage compositions determined by chemical analysis.

* Calculated from Pickering's results, J. Chem. Soc. *57*, 363 (1890).

AUTHORITIES — W. C. FERGUSON; H. P. TALBOT.

This table has been approved and adopted as a standard by the Manufacturing Chemists' Association of the United States.

W. H. BOWER,
HENRY HOWARD,
JAS. L. MORGAN,
ARTHUR WYMAN,
A. G. ROSENGARTEN,
Executive Committee

New York, June 23, 1904.

Degrees Baumé.	Specific Gravity $\frac{60°}{60°}$ F.	Degrees Twaddell.	Per Cent H_2SO_4.	Weight of 1 Cu. Ft. in Lbs. Av.	Per Cent O. V.	Pounds O. V. in 1 Cubic Foot.
25	1.2083	41.7	28.28	75.36	30.34	22.87
26	1.2185	43.7	29.53	76.00	31.69	24.08
27	1.2288	45.8	30.79	76.64	33.04	25.32
28	1.2393	47.9	32.05	77.30	34.39	26.58
29	1.2500	50.0	33.33	77.96	35.76	27.88
30	1.2609	52.2	34.63	78.64	37.16	29.22
31	1.2719	54.4	35.93	79.33	38.55	30.58
32	1.2832	56.6	37.26	80.03	39.98	32.00
33	1.2946	58.9	38.58	80.74	41.40	33.42
34	1.3063	61.3	39.92	81.47	42.83	34.90
35	1.3182	63.6	41.27	82.22	44.28	36.41
36	1.3303	66.1	42.63	82.97	45.74	37.95
37	1.3426	68.5	43.99	83.74	47.20	39.53
38	1.3551	71.0	45.35	84.52	48.66	41.13
39	1.3679	73.6	46.72	85.32	50.13	42.77
40	1.3810	76.2	48.10	86.13	51.61	44.45
41	1.3942	78.8	49.47	86.96	53.08	46.16
42	1.4078	81.6	50.87	87.80	54.58	47.92
43	1.4216	84.3	52.26	88.67	56.07	49.72
44	1.4356	87.1	53.66	89.54	57.58	51.56
45	1.4500	90.0	55.07	90.44	59.09	53.44
46	1.4646	92.9	56.48	91.35	60.60	55.36
47	1.4796	95.9	57.90	92.28	62.13	57.33
48	1.4948	99.0	59.32	93.23	63.65	59.34
49	1.5104	102.1	60.75	94.20	65.18	61.40
50	1.5263	105.3	62.18	95.20	66.72	63.52
51	1.5426	108.5	63.66	96.21	68.31	65.72
52	1.5591	111.8	65.13	97.24	69.89	67.96
53	1.5761	115.2	66.63	98.30	71.50	70.28
54	1.5934	118.7	68.13	99.38	73.11	72.66
55	1.6111	122.2	69.65	100.48	74.74	75.10
56	1.6292	125.8	71.17	101.61	76.37	77.60
57	1.6477	129.5	72.75	102.77	78.07	80.23
58	1.6667	133.3	74.36	103.95	79.79	82.95
59	1.6860	137.2	75.99	105.16	81.54	85.75

X.—SULFURIC ACID (Continued)

ALLOWANCE FOR TEMPERATURE

At	10°	Bé.	.029° Bé.	or	.00023	Sp. Gr.	= 1° F.
"	20°	"	.036°	"	.00034	"	= 1° "
"	30°	"	.035°	"	.00039	"	= 1° "
"	40°	"	.031°	"	.00041	"	= 1° "
"	50°	"	.028°	"	.00045	"	= 1° "
"	60°	"	.026°	"	.00053	"	= 1° "
"	63°	"	.026°	"	.00057	"	= 1° "
"	66°	"	.0235°	"	.00054	"	= 1° "

Degrees Baumé.	* Freezing (Melting) Point. °F.	Per Cent 60° Baumé.	Pounds 60° Baumé in 1 Cubic Foot.	Per Cent 50° Baumé.	Pounds 50° Baumé in 1 Cubic Foot.
25	−23				
26	−30				
27	−39				
28	−49				
29	−61				
30	−74				
31	−82				
32	−96				
33	−97				
34	−91				
35	−81				
36	−70				
37	−60				
38	−53				
39	−47				
40	−41	61.93	53.34	77.36	66.63
41	−35	63.69	55.39	79.56	69.19
42	−31	65.50	57.50	81.81	71.83
43	−27	67.28	59.66	84.05	74.53
44	−23	69.09	61.86	86.30	77.27
45	−20	70.90	64.12	88.56	80.10
46	−14	72.72	66.43	90.83	82.98
47	−15	74.55	68.79	93.12	85.93
48	−18	76.37	71.20	95.40	88.94
49	−22	78.22	73.68	97.70	92.03
50	−27	80.06	76.21	100.00	95.20
51	−33	81.96	78.85	102.38	98.50
52	−39	83.86	81.54	104.74	101.85
53	−49	85.79	84.33	107.15	105.33
54	−59	87.72	87.17	109.57	108.89
55	.. Below 40	89.67	90.10	112.01	112.55
56	..	91.63	93.11	114.46	116.30
57	..	93.67	96.26	117.00	120.24
58	..	95.74	99.52	119.59	124.31
59	−7	97.84	102.89	122.21	128.52

X.—SULFURIC ACID (Continued)

Degrees Baumé.	Specific Gravity $\frac{60° F.}{60°}$	Degrees Twaddell.	Per Cent H_2SO_4.	Weight of 1 Cu. Ft. in Lbs. Av.	Per Cent O. V.	Pounds O. V. in 1 Cubic Foot.
60	1.7059	141.2	77.67	106.40	83.35	88.68
61	1.7262	145.2	79.43	107.66	85.23	91.76
62	1.7470	149.4	81.30	108.96	87.24	95.06
63	1.7683	153.7	83.34	110.29	89.43	98.63
64	1.7901	158.0	85.66	111.65	91.92	102.63
64¼	1.7957	159.1	86.33	112.00	92.64	103.75
64½	1.8012	160.2	87.04	112.34	93.40	104.93
64¾	1.8068	161.4	87.81	112.69	94.23	106.19
65	1.8125	162.5	88.65	113.05	95.13	107.54
65¼	1.8182	163.6	89.55	113.40	96.10	108.97
65½	1.8239	164.8	90.60	113.76	97.22	110.60
65¾	1.8297	165.9	91.80	114.12	98.51	112.42
66	1.8354	167.1	93.19	114.47	100.00	114.47

Degrees Baumé.	Freezing (Melting) Point.	Per Cent 60° Baumé.	Pounds 60° Baumé in Cubic Foot.	Per Cent 50° Baumé.	Pounds 50° Baumé in Cubic Foot.
60	+12.6	100.00	106.40	124.91	132.91
61	27.3	102.27	110.10	127.74	137.52
62	39.1	104.67	114.05	130.75	142.47
63	46.1	107.30	118.34	134.03	147.82
64	46.4	110.29	123.14	137.76	153.81
64¼	43.6	111.15	124.49	138.84	155.50
64½	41.1	112.06	125.89	139.98	157.25
64¾	37.9	113.05	127.40	141.22	159.14
65	33.1	114.14	129.03	142.57	161.17
65¼	24.6	115.30	130.75	144.02	163.32
65½	13.4	116.65	132.70	145.71	165.76
65¾	− 1	118.19	134.88	147.63	168.48
66	−29	119.98	137.34	149.87	171.56

XI.—SULFURIC ACID TABLE
94–100% H_2SO_4
By H. B. Bishop

Bé.	Sp. Gr. at 60° F.	Per Cent. H_2SO_4	Wt. 1 Cu. Ft.	Allowance for Temperature.
66	1.8354	93.19	114.47	At 94% .00054 sp.gr. = 1° F.
66.12	1.8381	94.00	114.64	" 96 .0053 " = 1° F.
66.23	1.8407	95.00	114.80	" 97.5 .00052 " = 1° F.
66.31	1.8427	96.00	114.93	" 100 .00052 " = 1° F.
66.36	1.8437	97.00	114.99	
66.36	1.8439	97.50	114.99	
66.36	1.8437	98.00	114.99	
66.30	1.8424	99.00	114.91	
66.16	1.8391	100.00	114.70	

FUMING SULFURIC ACID EQUIVALENTS

Total SO_3	Equivalent H_2SO_4	Per Cent H_2SO_4	Per Cent Free SO_3	Total SO_3	Equivalent H_2SO_4	Per Cent H_2SO_4	Per Cent Free SO_3
81.63	100.00	100	0	90.82	111.25	50	50
81.82	100.23	99	1	91.00	111.48	49	51
82.00	100.45	98	2	91.18	111.70	48	52
82.18	100.67	97	3	91.37	111.93	47	53
82.37	100.90	96	4	91.55	112.15	46	54
82.55	101.13	95	5	91.73	112.37	45	55
82.73	101.35	94	6	91.92	112.60	44	56
82.92	101.58	93	7	92.10	112.82	43	57
83.10	101.80	92	8	92.29	113.05	42	58
83.29	102.03	91	9	92.47	113.28	41	59
83.47	102.25	90	10	92.65	113.50	40	60
83.65	102.47	89	11	92.84	113.73	39	61
83.84	102.70	88	12	93.02	113.95	38	62
84.02	102.92	87	13	93.20	114.17	37	63
84.20	103.15	86	14	93.39	114.40	36	64
84.39	103.38	85	15	93.57	114.62	35	65
84.57	103.60	84	16	93.76	114.85	34	66
84.75	103.82	83	17	93.94	115.08	33	67
84.94	104.05	82	18	94.12	115.30	32	68
85.12	104.27	81	19	94.31	115.53	31	69
85.31	104.50	80	20	94.49	115.75	30	70
85.49	104.73	79	21	94.67	115.97	29	71
85.67	104.95	78	22	94.86	116.20	28	72
85.86	105.18	77	23	95.04	116.42	27	73
86.04	105.40	76	24	95.22	116.65	26	74
86.22	105.62	75	25	95.41	116.88	25	75
86.41	105.85	74	26	95.59	117.10	24	76
86.59	106.07	73	27	95.78	117.33	23	77
86.78	106.30	72	28	95.96	117.55	22	78
86.96	106.53	71	29	96.14	117.77	21	79
87.14	106.75	70	30	96.33	118.00	20	80
87.33	106.98	69	31	96.51	118.22	19	81
87.51	107.20	68	32	96.69	118.45	18	82
87.69	107.42	67	33	96.88	118.68	17	83
87.88	107.65	66	34	97.06	118.90	16	84
88.06	107.87	65	35	97.25	119.13	15	85
88.24	108.10	64	36	97.43	119.35	14	86
88.43	108.33	63	37	97.61	119.57	13	87
88.61	108.55	62	38	97.80	119.80	12	88
88.80	108.78	61	39	97.98	120.03	11	89
88.98	109.00	60	40	98.16	120.25	10	90
89.16	109.22	59	41	98.35	120.48	9	91
89.35	109.45	58	42	98.53	120.70	8	92
89.53	109.67	57	43	98.71	120.92	7	93
89.71	109.90	56	44	98.90	121.15	6	94
89.90	110.13	55	45	99.08	121.37	5	95
90.08	110.35	54	46	99.27	121.60	4	96
90.27	110.58	53	47	99.45	121.83	3	97
90.45	110.80	52	48	99.63	122.05	2	98
90.63	111.02	51	49	99.82	122.28	1	99
				100.00	122.50	0	100

Compiled from the table by H. B. Bishop, Van Nostrand's Chemical Annual, 1918.

XII.—ACETIC ACID AT 15°

OUDEMANS

Specific Gravity.	Per Cent $H.C_2H_3O_2$.	Specific Gravity.	Per Cent $H.C_2H_3O_2$.	Specific Gravity.	Per Cent $H.C_2H_3O_2$.	Specific Gravity.	Per Cent $H.C_2H_3O_2$.
0.9992	0	1.0363	26	1.0623	51	1.0747	76
1.0007	1	1.0375	27	1.0631	52	1.0748	77
1.0022	2	1.0388	28	1.0638	53	1.0748	78
1.0037	3	1.0400	29	1.0646	54	1.0748	79
1.0052	4	1.0412	30	1.0653	55	1.0748	80
1.0067	5	1.0424	31	1.0660	56	1.0747	81
1.0083	6	1.0436	32	1.0666	57	1.0746	82
1.0098	7	1.0447	33	1.0673	58	1.0744	83
1.0113	8	1.0459	34	1.0679	59	1.0742	84
1.0127	9	1.0470	35	1.0685	60	1.0739	85
1.0142	10	1.0481	36	1.0691	61	1.0736	86
1.0157	11	1.0492	37	1.0697	62	1.0731	87
1.0171	12	1.0502	38	1.0702	63	1.0726	88
1.0185	13	1.0513	39	1.0707	64	1.0720	89
1.0200	14	1.0523	40	1.0712	65	1.0713	90
1.0214	15	1.0533	41	1.0717	66	1.0705	91
1.0228	16	1.0543	42	1.0721	67	1.0696	92
1.0242	17	1.0552	43	1.0725	68	1.0686	93
1.0256	18	1.0562	44	1.0729	69	1.0674	94
1.0270	19	1.0571	45	1.0733	70	1.0660	95
1.0284	20	1.0580	46	1.0737	71	1.0644	96
1.0298	21	1.0589	47	1.0740	72	1.0625	97
1.0311	22	1.0598	48	1.0742	73	1.0604	98
1.0324	23	1.0607	49	1.0744	74	1.0580	99
1.0337	24	1.0615	50	1.0746	75	1.0553	100
1.0350	25						

XIII.—MELTING POINTS OF ACETIC ACID

RUDORFF, Ber. 3, 390. (1870).

100 gr. $H.C_2H_3O_2$ mixed with gr. water.	100 parts by weight contain parts water.	Melting (solidifying) point °C.	100 gr. $H.C_2H_3O_2$ mixed with gr. water.	100 parts by weight contain parts water.	Melting (solidifying) point °C.
0.0	0.0	16.7°	8.0	7.407	6.25°
0.5	0.497	15.65	9.0	8.257	5.3
1.0	0.990	14.8	10.0	9.090	4.3
1.5	1.477	14.0	11.0	9.910	3.6
2.0	1.961	13.25	12.0	10.774	2.7
3.0	2.912	11.95	15.0	13.043	−0.2
4.0	3.846	10.5	18.0	15.324	−2.6
5.0	4.761	9.4	21.0	17.355	−5.1
6.0	5.660	8.2	24.0	19.354	−7.4
7.0	6.542	7.1			

Boiling point 100% acid 117.8°.

XIV.—AQUA AMMONIA

According to W. C. Ferguson

Degrees Baumé.	Sp. Gr. $\frac{60^\circ}{60^\circ}$ F.	Per Cent NH_3.	Degrees Baumé.	Sp. Gr. $\frac{60^\circ}{60^\circ}$ F.	Per Cent NH_3.	Degrees Baumé.	Sp. Gr. $\frac{60^\circ}{60^\circ}$ F.	Per Cent NH_3.
10.00	1.0000	.00	16.50	.9556	11.18	23.00	.9150	23.52
10.25	.9982	.40	16.75	.9540	11.64	23.25	.9135	24.01
10.50	.9964	.80	17.00	.9524	12.10	23.50	.9121	24.50
10.75	.9947	1.21	17.25	.9508	12.56	23.75	.9106	24.99
11.00	.9929	1.62	17.50	.9492	13.02	24.00	.9091	25.48
11.25	.9912	2.04	17.75	.9475	13.49	24.25	.9076	25.97
11.50	.9894	2.46	18.00	.9459	13.96	24.50	.9061	26.46
11.75	.9876	2.88	18.25	.9444	14.43	24.75	.9047	26.95
12.00	.9859	3.30	18.50	.9428	14.90	25.00	.9032	27.44
12.25	.9842	3.73	18.75	.9412	15.37	25.25	.9018	27.93
12.50	.9825	4.16	19.00	.9396	15.84	25.50	.9003	28.42
12.75	.9807	4.59	19.25	.9380	16.32	25.75	.8989	28.91
13.00	.9790	5.02	19.50	.9365	16.80	26.00	.8974	29.40
13.25	.9773	5.45	19.75	.9349	17.28	26.25	.8960	29.89
13.50	.9756	5.88	20.00	.9333	17.76	26.50	.8946	30.38
13.75	.9739	6.31	20.25	.9318	18.24	26.75	.8931	30.87
14.00	.9722	6.74	20.50	.9302	18.72	27.00	.8917	31.36
14.25	.9705	7.17	20.75	.9287	19.20	27.25	.8903	31.85
14.50	.9689	7.61	21.00	.9272	19.68	27.50	.8889	32.34
14.75	.9672	8.05	21.25	.9256	20.16	27.75	.8875	32.83
15.00	.9655	8.49	21.50	.9241	20.64	28.00	.8861	33.32
15.25	.9639	8.93	21.75	.9226	21.12	28.25	.8847	33.81
15.50	.9622	9.38	22.00	.9211	21.60	28.50	.8833	34.30
15.75	.9605	9.83	22.25	.9195	22.08	28.75	.8819	34.79
16.00	.9589	10.28	22.50	.9180	22.56	29.00	.8805	35.28
16.25	.9573	10.73	22.75	.9165	23.04			

ALLOWANCE FOR TEMPERATURE

The coefficient of expansion for ammonia solutions, varying with the temperature, correction must be applied according to the following table:

Corrections to be Added for Each Degree Below 60° F.			Corrections to be Subtracted for Each Degree Above 60° F.			
Degrees Baumé.	40° F.	50° F.	70° F.	80° F.	90° F.	100° F.
14° Bé	.015° Bé	.017° Bé	.020° Bé	.022° Bé	.024° Bé	.026° Bé
16°	.021 "	.023 "	.026 "	.028 "	.030 "	.032 "
18°	.027 "	.029 "	.031 "	.033 "	.035 "	.037 "
20°	.033 "	.036 "	.037 "	.038 "	.040 "	.042 "
22°	.039 "	.042 "	.043 "	.045 "	.047 "	
26°	.053 "	.057 "	.057 "	.059 "		

XV.—SODIUM HYDROXIDE SOLUTION AT 15°

Lunge

Specific Gravity.	Degrees Baume.	Degrees Twaddell.	Per Cent Na_2O.	Per Cent NaOH.	1 Liter contains Grams	
					Na_2O.	NaOH
1.007	1.0	1.4	0.47	0.61	4	6
1.014	2.0	2.8	0.93	1.20	9	12
1.022	3.1	4.4	1.55	2.00	16	21
1.029	4.1	5.8	2.10	2.70	22	28
1.036	5.1	7.2	2.60	3.35	27	35
1.045	6.2	9.0	3.10	4.00	32	42
1.052	7.2	10.4	3.60	4.64	38	49
1.060	8.2	12.0	4.10	5.29	43	56
1.067	9.1	13.4	4.55	5.87	49	63
1.075	10.1	15.0	5.08	6.55	55	70
1.083	11.1	16.6	5.67	7.31	61	79
1.091	12.1	18.2	6.20	8.00	68	87
1.100	13.2	20.0	6.73	8.68	74	95
1.108	14.1	21.6	7.30	9.42	81	104
1.116	15.1	23.2	7.80	10.06	87	112
1.125	16.1	25.0	8.50	10.97	96	123
1.134	17.1	26.8	9.18	11.84	104	134
1.142	18.0	28.4	9.80	12.64	112	144
1.152	19.1	30.4	10.50	13.55	121	156
1.162	20.2	32.4	11.14	14.37	129	167
1.171	21.2	34.2	11.73	15.13	137	177
1.180	22.1	36.0	12.33	15.91	146	183
1.190	23.1	38.0	13.00	16.77	155	200
1.200	24.2	40.0	13.70	17.67	164	212
1.210	25.2	42.0	14.40	18.58	174	225
1.220	26.1	44.0	15.18	19.58	185	239
1.231	27.2	46.2	15.96	20.59	196	253
1.241	28.2	48.2	16.76	21.42	208	266
1.252	29.2	50.4	17.55	22.64	220	283
1.263	30.2	52.6	18.35	23.67	232	299
1.274	31.2	54.8	19.23	24.81	245	316
1.285	32.2	57.0	20.00	25.80	257	332
1.297	33.2	59.4	20.80	26.83	270	348
1.308	34.1	61.6	21.55	27.80	282	364
1.320	35.2	64.0	22.35	28.83	295	381
1.332	36.1	66.4	23.20	29.93	309	399
1.345	37.2	69.0	24.20	31.22	326	420

XV.—SODIUM HYDROXIDE SOLUTION AT 15° (Continued)

Specific Gravity.	Degrees Baumé.	Degrees Twaddell.	Per Cent Na_2O.	Per Cent NaOH.	1 Liter contains Grams	
					Na_2O.	NaOH
1.357	38.1	71.4	25.17	32.47	342	441
1.370	39.2	74.0	26.12	33.69	359	462
1.383	40.2	76.6	27.10	34.96	375	483
1.397	41.2	79.4	28.10	36.25	392	506
1.410	42.2	82.0	29.05	37.47	410	528
1.424	43.2	84.8	30.08	38.80	428	553
1.438	44.2	87.6	31.00	39.99	446	575
1.453	45.2	90.6	32.10	41.41	466	602
1.468	46.2	93.6	33.20	42.83	487	629
1.483	47.2	96.6	34.40	44.38	510	658
1.498	48.2	99.6	35.70	46.15	535	691
1.514	49.2	102.8	36.90	47.60	559	721
1.530	50.2	106.0	38.00	49.02	581	750

XVI.—VAPOR TENSION OF WATER IN MILLIMETERS OF MERCURY −2° TO +36° C.

According to Regnault, Broch, and Weibe

°C.	0	.1	.2	.3	.4	.5	.6	.7	.8	.9
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
−2	3.958	3.929	3.900	3.872	3.844	3.815	3.787	3.760	3.732	3.705
−1	4.258	4.227	4.197	4.166	4.136	4.106	4.076	4.046	4.016	3.987
−0	4.579	4.546	4.513	4.481	4.448	4.416	4.384	4.352	4.321	4.289
0	4.579	4.612	4.646	4.679	4.713	4.747	4.782	4.816	4.851	4.886
1	4.921	4.957	4.992	5.028	5.064	5.101	5.137	5.174	5.211	5.248
2	5.286	5.324	5.362	5.400	5.438	5.477	5.516	5.555	5.595	5.635
3	5.675	5.715	5.755	5.796	5.837	5.878	5.920	5.961	6.003	6.046
4	6.088	6.131	6.174	6.217	6.261	6.305	6.349	6.393	6.438	6.482
5	6.528	6.574	6.620	6.666	6.712	6.759	6.806	6.853	6.901	6.949
6	6.997	7.045	7.094	7.143	7.192	7.242	7.292	7.342	7.392	7.443
7	7.494	7.546	7.598	7.650	7.702	7.755	7.808	7.861	7.914	7.968
8	8.023	8.077	8.132	8.187	8.243	8.299	8.355	8.412	8.469	8.526
9	8.584	8.642	8.700	8.759	8.818	8.877	8.937	8.997	9.057	9.118
10	9.179	9.240	9.302	9.364	9.427	9.490	9.553	9.616	9.680	9.745
11	9.810	9.875	9.940	10.006	10.072	10.139	10.206	10.274	10.342	10.410
12	10.479	10.548	10.617	10.687	10.757	10.828	10.899	10.970	11.042	11.114
13	11.187	11.260	11.333	11.407	11.481	11.556	11.631	11.706	11.782	11.859
14	11.936	12.013	12.091	12.169	12.247	12.326	12.406	12.486	12.566	12.647
15	12.728	12.810	12.892	12.974	13.057	13.141	13.225	13.309	13.394	13.480
16	13.565	13.651	13.738	13.825	13.913	14.001	14.090	14.179	14.269	14.359
17	14.450	14.541	14.632	14.724	14.817	14.910	15.003	15.097	15.192	15.287
18	15.383	15.479	15.575	15.672	15.770	15.868	15.967	16.066	16.166	16.266
19	16.367	16.469	16.571	16.673	16.776	16.880	16.984	17.088	17.193	17.299
20	17.406	17.513	17.620	17.728	17.837	17.947	18.057	18.167	18.278	18.390
21	18.503	18.616	18.729	18.844	18.959	19.074	19.190	19.307	19.424	19.542
22	19.661	19.780	19.900	20.021	20.142	20.264	20.386	20.510	20.634	20.758
23	20.883	21.010	21.137	21.264	21.393	21.522	21.652	21.782	21.913	22.045
24	22.178	22.311	22.446	22.581	22.716	22.853	22.990	23.128	23.266	23.406
25	23.546	23.686	23.828	23.970	24.113	24.257	24.401	24.547	24.693	24.839
26	24.987	25.135	25.284	25.434	25.584	25.736	25.888	26.041	26.195	26.349
27	26.505	26.661	26.818	26.976	27.134	27.294	27.454	27.615	27.777	27.939
28	28.103	28.267	28.432	28.599	28.766	28.933	29.102	29.271	29.442	29.613
29	29.785	29.958	30.132	30.307	30.482	30.659	30.836	31.015	31.194	31.374
30	31.555	31.737	31.919	32.103	32.288	32.473	32.660	32.847	33.036	33.225
31	33.416	33.607	33.799	33.992	34.187	34.382	34.578	34.775	34.973	35.172
32	35.372	35.573	35.775	35.978	36.182	36.387	36.593	36.800	37.008	37.217
33	37.427	37.638	37.851	38.064	38.278	38.493	38.710	38.927	39.146	39.365
34	39.586	39.807	40.030	40.254	40.479	40.705	40.933	41.161	41.390	41.621
35	41.583	42.085	42.319	42.554	42.791	43.028	43.266	43.506	43.747	43.989

XVII.—USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS *

Substance	Formula	Molecular or Atomic Weight	Normal Coefficient 1 ml. = g.	Solubility in 100 G. Water	Indicator
Acetic acid	$HC_2H_3O_2$	60.03	.06003		
anhydride	$(CH_3CO)_2O$	102.07	.051035		
Aluminium	Al	26.97	.008990		
chloride	Al_2Cl_6	266.68	.04445	$69.87^{15°}$	P.
chloride	$Al_2Cl_6 \cdot 12H_2O$	482.87	.08048	40	P.
oxide	Al_2O_3	101.94	.01699	insol.	
phosphate	$AlPO_4$	121.99	.04066		
sulfate	$Al_2(SO_4)_3$	342.12	.05706	$36.1^{20°}$	P.
sulfate	$Al_2(SO_4)_3 \cdot 18H_2O$	666.40	.11107	87	P.
Ammonia	NH_3	17.03	.01703	....	M.
Ammonium	NH_4	18.04	.01804	....	M.
chloride	NH_4Cl	53.50	.05350	$29.4^{0°}$	M.
hydroxide	NH_4OH	35.05	.03505	....	M.
nitrate	NH_4NO_3	80.05	.08005	$118^{0°}$	M.
oxalate	$(NH_4)_2C_2O_4 \cdot H_2O$	142.09	.07105‡		
sulfate	$(NH_4)_2SO_4$	132.14	.06607	$71^{0°}$	M.
Antimony	Sb	121.76	.06088		
chloride (tri)	$SbCl_3$	228.13	.11456 §		
chloride (penta)	$SbCl_5$	299.05	.14953 §		
oxide (tri)	Sb_2O_3	291.52	.07288 §		
oxide (penta)	Sb_2O_5	323.52	.08088 §		
Arsenic	As	74.93	.03746		
oxide	As_2O_5	229.86	.03832 †	150	
oxide	As_2O_5	229.86	.05748 §		
Arsenious oxide	As_2O_3	197.36	.03299	$1.7^{16°}$	
Arsenious oxide	As_2O_3	197.36	.04948 §	$1.7^{16°}$	
Barium	Ba	137.36	.06868		
carbonate	$BaCO_3$	197.36	.09868	$.0022^{20°}$	M.
chloride	$BaCl_2$	208.27	.10414	$30.9^{0°}$	
chloride	$BaCl_2 \cdot 2H_2O$	244.31	.12216	$36.2^{0°}$	
hydroxide	$Ba(OH)_2$	171.38	.08560		
hydroxide	$Ba(OH)_2 \cdot 8H_2O$	315.50	.15775	$5.15^{15°}$	
oxalate	$BaC_2O_4 \cdot H_2O$	243.37	.12168		
oxide	BaO	153.36	.07668	$1.5^{0°}$	
sulfate	$BaSO_4$	233.42	.11671	$.000172^{0°}$	
sulfite	$BaSO_3$	217.43	.10872		
peroxide	BaO_2	169.36	.08469 §	insol.	
Boric acid	H_3BO_3	61.85	.06185		
Bromine	Br	79.92	.07992	$4.17^{0°}$	
Cadmium carbonate	$CdCO_3$	172.41	.08620	insol.	
chloride	$CdCl_2$	183.32	.09166	$140^{20°}$	
chloride	$CdCl_2 \cdot 2\frac{1}{2}H_2O$	228.36	.11418	$168^{20°}$	
sulfide	CdS	144.47	.07223	insol.	
Calcium	Ca	40.08	.02004		
acetate	$Ca(C_2H_3O_2)_2$	158.13	.07907		
bicarbonate	$Ca(HCO_3)_2$	162.09	.08105		
carbonate	$CaCO_3$	100.075	.05004	.0013	M.
chloride	$CaCl_2$	110.99	.05550	$59.5^{0°}$	
chloride	$CaCl_2 \cdot 6H_2O$	219.09	.10954	$117.4^{0°}$	
fluoride	CaF_2	78.08	.03904		
hydroxide	$Ca(OH)_2$	74.09	.037045	$.17^{0°}$	
oxalate	$CaC_2O_4 \cdot H_2O$	146.10	.07305		

* Compiled and arranged by R. M. Meiklejohn.
† Precipitation reagents. ‡ Acids and bases. § Oxidizing and reducing agents.
M. Methyl orange. P. Phenolphthalein. Temp. C.

XVII.—USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS (*Continued*)

Substance	Formula	Molecular or Atomic Weight	Normal Coefficient 1 ml. = g.	Solubility in 100 G. Water	Indicator
Calcium oxide	CaO	56.08	.02804	$.13^{0^\circ}$	
sulfate	$CaSO_4$	136.13	.06807	$.179^{0^\circ}$	
sulfide	CaS	72.14	.03607	$.15^{10^\circ}$	
Carbon	C	12.00	.00300	insol.	
dioxide	CO_2	44.00	.02200†	179.67 ml.$^{0^\circ}$	
dioxide	CO_2	44.00	.04400‡	179.67 ml.$^{0^\circ}$	P.
Chlorine	Cl	35.46	.03546	150 ml.$^{0^\circ}$	
Chromic anhydride	CrO_3	100.01	.03334§	163.40^{0°	
oxide	Cr_2O_3	152.02	.02534§	insol.	
Citric acid	$H_3C_6H_5O_7$	192.06	.06402	133.	
Cobalt	Co	58.94	.02947		
Copper	Cu	63.57	.03178		
oxide	CuO	79.57	.07957		
sulfate	$CuSO_4$	159.63	.15963	20^{0°	
sulfate	$CuSO_4 \cdot 5H_2O$	249.71	.24971	31.61^{0°	
sulfide	CuS	95.63	.04781	.000033	
Cyanogen	CN	26.02	.02602		
Ferric oxide	Fe_2O_3	159.68	.07984§		
phosphate	$FePO_4 \cdot 4H_2O$	222.92	.07431		
Ferrous oxide	FeO	71.84	.07184§	insol.	
sulfate	$FeSO_4$	151.90	.15190§		
sulfate	$FeSO_4 \cdot 7H_2O$	278.01	.27801§	32.8^{0°	
ammonium sulfate	$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$	392.54	.39215	18^{0°	
Formic acid	$HCOOH$	46.02	.04602		
Hydrobromic acid	HBr	80.92	.08092	221.2^{0°	
Hydrochloric acid	HCl	36.47	.03647	82.5^{10°	
Hydrocyanic acid	HCN	27.02	.02702		
Hydrofluoric acid	HF	20.01	.02001	264	
Hydrofluosilicic acid	H_2SiF_6	144.32	.02405‡		
Hydroiodic acid	HI	127.94	.12794		
Hydrogen peroxide	H_2O_2	34.02	.01701		
Hydrogen sulfide	H_2S	34.08	.01704	437 ml.$^{0^\circ}$	
Iodine	I	126.92	.12692	$.0182^{11^\circ}$	
Iron	Fe	55.84	.05584		
Lead	Pb	207.22	.10361		
carbonate	$PbCO_3$	267.22	.13361	.00198	M.
chromate	$PbCrO_4$	323.23	.16161	$.00002^{18^\circ}$	
oxide	PbO	223.22	.11161		
peroxide	PbO_2	239.22	.11961		
sulfate	$PbSO_4$	303.28	.15164		
sulfide	PbS	239.28	.11964	.0001	
sulfite	$PbSO_3$	287.28	.14364†		
Magnesium	Mg	24.32	.01216		
carbonate	$MgCO_3$	84.32	.04216	.0106	
chloride	$MgCl_2$	95.23	.04762	52.2^{0°	M.
chloride	$MgCl_2 \cdot 6H_2O$	203.33	.10167	167	M.
oxide	MgO	40.32	.02016	.00062	M.
sulfate	$MgSO_4$	120.38	.06019	26.9^{0°	M.
sulfate	$MgSO_4 \cdot 7H_2O$	246.49	.12324	76.9^{0°	M.
Malic acid	$H_2C_4H_4O_5$	134.05	.06703		
Manganese	Mn	54.93	.02746		
chloride	$MnCl_2$	125.85	.06292	62.16^{10°	
peroxide	MnO_2	86.93	.04346	insol.	

† Precipitation reagents. ‡ Acids and bases. § Oxidizing and reducing agents.
M. Methyl orange. P. Phenolphthalein. Temp. C.

XVII.—USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS (*Continued*)

Substance	Formula	Molecular or Atomic Weight	Normal Coefficient 1 ml. = g.	Solubility in 100 G. Water	Indicator
Manganese sulfate	$MnSO_4$	150.99	.075495	53.2^0°	
Mercuric chloride	$HgCl_2$	271.52	.13576	5.73^0°	
Mercurous chloride	HgCl	236.07	.23607§		
Mercury	Hg	200.6	.2006		
Nickel	Ni	58.69	.02934		
Nitric acid	HNO_3	63.02	.06302‡		
Nitric acid	HNO_3	63.02	.021006§		
Nitrogen trioxide	N_2O_3	76.02	.019005§		
pentoxide	N_2O_5	108.02	.05401‡		
pentoxide	N_2O_5	108.02	.018033§		
Nitrous acid	HNO_2	47.02	.04702		
Nitrogen	N	14.01	.01401		
Oxalic acid	$H_2C_2O_4$	90.03	.04501		
Oxalic acid	$H_2C_2O_4 \cdot 2H_2O$	126.06	.06303	4.9^0°	
Phosphoric acid	H_3PO_4	98.06	.09806‡	v. sol.	M.
Phosphoric acid	H_3PO_4	98.04	.04902‡	v. sol. 0	P.
Phosphoric acid	H_3PO_4	98.04	.03266	v. sol.	
Phosphorous acid (ortho)	H_3PO_3	82.04	.02735		
pentoxide	P_2O_5	142.04	.02367		
Potassium	K	39.10	.03910		
bicarbonate	$KHCO_3$	100.11	.10011	22.4^0°	M.
bitartrate	$KHC_4H_4O_6$	188.14	.18814	.37^0°	P.
bromate	$KBrO_3$	167.02	.16702		
bi-iodate	$KH(IO_3)_2$	389.95	.38995‡		
bi-iodate	$KH(IO_3)_2$	389.97	.03249§		
bromide	KBr	119.02	.11902	53.48^0°	
carbonate	K_2CO_3	138.20	.06910	89.4^0°	M.
carbonate	K_2CO_3	138.20	.06910‡		
chlorate	$KClO_3$	122.56	.020427§	3.3^0°	
chloride	KCl	74.56	.07456	28.5^0°	
chromate	K_2CrO_4	194.21	.06474§	61.5^0°	
cyanide	KCN	65.11	.06511†	v. sol.	
dichromate	$K_2Cr_2O_7$	294.22	.07355†		
dichromate	$K_2Cr_2O_7$	294.22	.14710‡	4.9^0°	P.
dichromate	$K_2Cr_2O_7$	294.22	.04903§	4.9^0°	
ferrocyanide	$K_4Fe(CN)_6$	368.31	.36832§		
ferrocyanide	$K_4Fe(CN)_6 \cdot 3H_2O$	422.33	.42237§	27.8^12°	
fluoride	KF	58.10	.05810		
hydroxide	KOH	56.11	.05611	107^15°	
iodate	KIO_3	214.03	.03567	4.74^0°	
iodide	KI	166.03	.16603	126.1^0°	
manganate	K_2MnO_4	197.13	.049283§		
nitrate	KNO_3	101.11	.033703	13.3^0°	
nitrite	KNO_2	85.11	.08511	300^15.5°	
oxalate	$K_2C_2O_4 \cdot H_2O$	184.22	.09211		
oxide	K_2O	94.20	.04710	v. sol.	
perchlorate	$KClO_4$	138.56	.01732§		
permanganate	$KMnO_4$	158.03	.031606	2.83^0°	
sulfide	K_2S	110.26	.05513	sol.	
thiocyanate	KCNS	97.17	.09717	177.2^0°	
tartrate	$K_2C_4H_4O_6$	226.22	.11311	sol.	
Silver	Ag	107.88	.10788		

† Precipitation reagents. ‡ Acids and bases. § Oxidizing and reducing agents.
M. Methyl orange. P. Phenolphthalein. Temp. C.

XVII.—USEFUL DATA OF THE MORE IMPORTANT INORGANIC COMPOUNDS (*Continued*)

Substance	Formula	Molecular or Atomic Weight	Normal Coefficient 1 ml. = g.	Solubility in 100 G. Water	Indicator
Silver bromide	$AgBr$	187.80	.18780		
chloride	$AgCl$	143.34	.14334		
nitrate	$AgNO_3$	169.89	.16989	$122^{0°}$	
Sodium	Na	23.00	.02300		
bromide	$NaBr$	102.91	.10291	$79.5^{0°}$	
bicarbonate	$NaHCO_3$	84.00	.08400	$6.90^{0°}$	M.
carbonate	Na_2CO_3	105.99	.05300	$7.1^{0°}$	M.
chlorate	$NaClO_3$	106.45	.01774§		
chloride	$NaCl$	58.45	.05845	$35.7^{0°}$	
cyanide	$NaCN$	49.01	.04901	sol.	
hydroxide	$NaOH$	40.00	.04000	$133.3^{16°}$	
iodide	NaI	149.93	.14993†	$158.7^{0°}$	
nitrate	$NaNO_3$	85.01	.02834	$72.9^{0°}$	
nitrite	$NaNO_2$	69.01	.06901	$83.3^{20°}$	
oxalate	$Na_2C_2O_4$	133.99	.06700	$3.22^{15.5°}$	
oxide	Na_2O	61.99	.03100	decomp.	
phosphate (mono)	NaH_2PO_4	120.06‡	.12006	v. sol.	M.
phosphate (disod)	Na_2HPO_4	142.03‡	.14203	....	P. or M.
phosphate (disod)	$Na_2HPO_4 \cdot 12H_2O$	358.21‡	.35821	$6.3^{0°}$	P. or M.
phosphate (trisod)	Na_3PO_4	164.02‡	.16402	....	P.
phosphate	$Na_3PO_4 \cdot 12H_2O$	380.20	.38020§		P.
sulfide	Na_2S	78.05	.03903	$15.4^{10°}$	
sulfite	Na_2SO_3	126.05	.06303		
thiosulfate	$Na_2S_2O_3 \cdot 5H_2O$	248.19	.24819	$74.7^{0°}$	
thiosulfate	$Na_2S_2O_3 \cdot 5H_2O$	248.19	.24819§		
Stannic oxide	SnO_2	150.70	.15070		
Stannous chloride	$SnCl_2$	189.61	.09481	$83.9^{0°}$	
chloride	$SnCl_2 \cdot 2H_2O$	225.65	.112825	$118.7^{0°}$	
oxide	SnO	134.70	.06735	insol.	
Sulfur dioxide	SO_2	64.06	.03203	7979 ml.$^{0°}$	
trioxide	SO_3	80.06	.04003		
Sulfuric acid	H_2SO_4	98.08	.04904		
Sulfurous acid	H_2SO_3	82.076	.04104‡		
Tartaric acid	$H_2C_4H_4O_6$	150.05	.07503	$115^{0°}$	
Tin	Sn	118.70	.05935		
Titanium chloride	$TiCl_3$	154.27	.15427§		
Zinc	Zn	65.38	.03769		
carbonate	$ZnCO_3$	125.38	.06269	$.001^{15°}$	
chloride	$ZnCl_2$	136.29	.068145	$209^{0°}$	
oxide	ZnO	81.38	.04069	.001	
sulfate	$ZnSO_4$	161.44	.080715	$43.02^{0°}$	
sulfate	$ZnSO_4 \cdot 7H_2O$	287.55	.143775	$115.2^{0°}$	
sulfide	ZnS	97.44	.04872	.00069	

† Precipitation reagents. ‡ Acids and bases. § Oxidizing and reducing agents.
M. Methyl orange. P. Phenolphthalein. Temp. C.

XVIII.—COMPARISON OF CENTIGRADE AND FAHRENHEIT SCALE

° C.	−100	−0	+0	+100	+200	+300	+400	+500	+600	+700	+800	+900	° C.
	°F.	F.	F.	F.	F.	F.	F.	F.	F.	F.	F.	F.	
0	−148	+ 32	32	+212	392	572	752	932	1112	1292	1472	1652	0
5	−157	+ 23	41	221	401	581	761	941	1121	1301	1481	1661	5
10	−166	+ 14	50	230	410	590	770	950	1130	1310	1490	1670	10
15	−175	+ 5	59	239	419	599	779	959	1139	1319	1499	1679	15
20	−184	− 4	68	248	428	608	788	968	1148	1328	1508	1688	20
25	−193	− 13	77	257	437	617	797	977	1157	1337	1517	1697	25
30	−202	− 22	86	266	446	626	806	986	1166	1346	1526	1706	30
35	−211	− 31	95	275	455	635	815	995	1175	1355	1535	1715	35
40	−220	− 40	104	284	464	644	824	1004	1184	1364	1544	1724	40
45	−229	− 49	113	293	473	653	833	1013	1193	1373	1553	1733	45
50	−238	− 58	122	302	482	662	842	1022	1202	1382	1562	1742	50
55	−247	− 67	131	311	491	671	851	1031	1211	1391	1571	1751	55
60	−256	− 76	140	320	500	680	860	1040	1220	1400	1580	1760	60
65	−265	− 85	149	329	509	689	869	1049	1229	1409	1589	1769	65
70	−274	− 94	158	338	518	698	878	1058	1238	1418	1598	1778	70
75	−283	−103	167	347	527	707	887	1067	1247	1427	1607	1787	75
80	−292	−112	176	356	536	716	896	1076	1256	1436	1616	1796	80
85	−301	−121	185	365	545	725	905	1085	1265	1445	1625	1805	85
90	−310	−130	194	374	554	734	914	1094	1274	1454	1634	1814	90
95	−319	−139	203	383	563	743	923	1103	1283	1463	1643	1823	95
100	−328	−148	+212	392	572	752	932	1112	1292	1472	1652	1832	100
° C.	−200	−100	+100	+200	+300	+400	+500	+600	+700	+800	+900	+1000	° C.

C.°	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
F.°	2012	2192	2372	2552	2732	2912	3092	3272	3452	3632

Degrees C.×1.8+32=Degrees F. Degrees F.−32÷1.8=Degrees C.

Absolute zero, −273° C. = −459° F.

Comparison of Centigrade and Fahrenheit Scale for Every 1° C. from 0° to 100° C.

C.	0	10	20	30	40	50	60	70	80	90	C.
	F.	F.	F.	F.	F.	F.	F.	F.	F.	F.	
0	32	50	68	86	104	122	140	158	176	194	0
1	33.8	51.8	69.8	87.8	105.8	123.8	141.8	159.8	177.8	195.8	1
2	35.6	53.6	71.6	89.6	107.6	125.6	143.6	161.6	179.6	197.6	2
3	37.4	55.4	73.4	91.4	109.4	127.4	145.4	163.4	181.4	199.4	3
4	39.2	57.2	75.2	93.2	111.2	129.2	147.2	165.2	183.2	201.2	4
5	41.0	59	77	95	113	131	149	167	185	203	5
6	42.8	60.8	78.8	96.8	114.8	132.8	150.8	168.8	186.8	204.8	6
7	44.6	62.6	80.6	98.6	116.6	134.6	152.6	170.6	188.6	206.6	7
8	46.4	64.4	82.4	100.4	118.4	136.4	154.4	172.4	190.4	208.4	8
9	48.2	66.2	84.2	102.2	120.2	138.2	156.2	174.2	192.2	210.2	9
C.	9	19	29	39	49	59	69	79	89	99	C.

100° C. = 212° F.

XIX.—A TABLE OF CONSTANTS

The United Gas

All Volumes of Gases and Vapors are Given at 60° F. and 30″ Pressure

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
									Heat of Combustion		
Name of Gas or Vapor	Symbol or Formula	Molecular Weight	Sp. Gravity Gas or Vapor at 60° F. Air = 1.0	Boiling-point ° Fahr.	Sp. Gravity Liquid at 60° F. Water = 1.0	Sp. Heat Eq. Wts. at Const. Pr. Water = 1.0	Cubic Feet per Pound	Weight 1 Cubic Foot in Pounds	Calories per Molecular Wt. in Grams	British Thermal Units Per Cu. Ft.	British Thermal Units Per Pound
Carbon to CO	C	12	0.8292	......	.....	.....	15.749	.06350	29,000	276.2	4,350
Carbon to CO_2	C	12	0.8292	......	.....	.....	15.749	.06350	96,960	923.5	14,544
Carbonic oxide	CO	28	0.9671	......	.....	0.2450	13.503	.07407	67,960	323.5	4,368
Hydrogen	H	1	0.0392	......	.....	3.0490	188.620	.00530	68,360	326.2	61,523
Methane	Paraffin Series C_nH_{2n+2} CH_4	16	0.5529	......	.....	0.5929	23.626	.04234	211,930	1000.0	23,838
Ethane	C_2H_6	30	1.0368	......	.....	.....	12.594	.07940	370,440	1704.4	22,226
Propane	C_3H_8	44	1.5206	− 13°	.....	.....	8.587	.11645	529,210	2521.0	21,051
Butane	C_4H_{10}	58	2.0045	+ 33°	.....	.....	6.514	.15350	687,190	3274.0	21,326
Pentane	C_5H_{12}	72	2.4883	+100°	0.6273	.....	5.248	.19055	847,110	4035.6	21,177
Hexane	C_6H_{14}	86	2.9721	+156°	0.6610	.....	4.393	.22760	999,200	4750.8	20,914
Ethylene	Olefin Series C_nH_{2n} C_2H_4	28	0.9676	......	.....	0.4040	13.495	.07410	333,350	1588.0	21,430
Propylene	C_3H_6	42	1.4514	......	.....	.....	8.997	.11115	492,740	2347.2	21,120
Butylene	C_4H_8	56	1.9353	+ 23°	.....	.....	6.747	.14820	650,620	3099.2	20,913
Amylene	C_5H_{10}	70	2.4191	+102°	0.6511	.....	5.398	.18525	807,630	3847.2	20,767
Acetylene	Acetyl. Series C_nH_{2n-2} C_2H_2	26	0.8984	......	.....	.....	14.534	.06880	310,050	1476.7	21,465
Allylene	C_3H_4	40	1.3823	......	.....	.....	9.447	.10585	467,550	2227.1	21,040
Crotonylene	C_4H_6	54	1.8661	+ 64°	.....	.....	6.998	.14290	....	.....	.....
Benzene	Aromat. Series C_nH_{2n-6} C_6H_6	78	2.6953	+177°	0.8840	0.3754	4.845	.20640	799,350	3807.5	18,447
Toluene	C_7H_8	92	3.1792	+230°	0.8720	.....	4.107	.24345	955,680	4552.0	18,699
Xylene	C_8H_{10}	106	3.6630	+287°	0.8692	.....	3.565	.28050	....	.....	.....
Mesitylene	C_9H_{12}	120	4.1468	+326°	.....	.....	3.149	.31755	1,282,310	6108.0	19,235
Naphthalene	$C_{10}H_8$	128	4.4230	+424.4°	1.1517	.....	2.952	.33870	....	.....	.....
Hydrogen sul.	H_2S	34	1.1760	......	.....	0.2123	11.096	.09012	140,900	672.2	7,549
Ammonia	NH_3	17	0.5888	......	.....	0.5083	22.173	.04509	90,500	432.8	9,598
Hydrocy. acid	HCN	27	0.9348	......	.....	.....	13.968	.07159	158,620	757.0	10,575
Cyanogen	C_2N_2	52	1.8000	......	.....	.....	7.258	.13779	259,620	1238.2	8,986
Carbon bi-sul.	CS_2	76	2.6298	+114.8°	.....	.....	4.965	.20139	265,130	1264.6	6,279
Methyl alcohol	CH_4O	32	1.1121	+131.2°	0.8027	.....	11.742	.08516	182,230	872.9	10,250
Ethyl alcohol	C_2H_6O	46	1.5894	+172.9°	0.7946	1.4534	8.218	.12172	340,530	1622.0	13,325
Carbonic acid	CO_2	44	1.5195	......	.....	0.2163	8.593	.11637	....	.....	.....
Water	H_2O	18	0.6217	+212°	1.0000	0.4805	21.004	.04761	....	.....	.....
Sulfur dioxide	SO_2	64	2.2128	......	.....	0.1553	5.901	.16945	....	.....	.....
Oxygen	O	16	1.1052	......	.....	0.2174	11.816	.08463	....	.....	.....
Nitrogen	N	14	0.9701	......	.....	0.2438	13.460	.07429	....	.....	.....
Air	....	..	1.0000	......	.....	0.2374	13.059	.07658	....	.....	.....

AUTHORITIES AND METH

In Column IX the figures given in Hempel's "Gas Analysis," p. 375, were selected for the fundamental weight of oxygen, nitrogen, hydrogen, carbonic oxide and air.

The formula used for the conversion to English units is—grams per liter at 0° C. and 760 mm. × .05922 = pounds per cu. ft. at 60° F. and 30″ pressure. The derivation of the factor employed is

$$.05922 = \frac{28.316 \times .0022046 \times 30.00 \times 492}{29.92 \times 520}.$$

The weights of the compound gases are calculated from these data by Avogadro's law.

Column IV is calculated by the formula: $\text{sp.gr.} = \dfrac{\text{wt. 1 cu. ft. gas}}{\text{wt. 1 cu. ft. air}}$, and the figures thus obtained agree with the theoretical formula: $\text{sp.gr.} = \dfrac{\text{mol. wt.}}{28.94}$.

FOR CERTAIN GASES AND VAPORS

IMPROVEMENT COMPANY

The Temperature of Products of Combustion is Reduced to 18° C. = 64.4° F.

XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	XXI	XXII	XXIII	XXIV	XXV	XXVI
Cu. Ft. per Cu. Ft. of Combustible					Pounds per Pound of Combustible					Heat of Formation at Const. Pres.			
Req. for Combustion		Products of Combustion			Req. for Combustion		Products of Combustion			Calories per Molecular Wt. in Grams	B.t.u.		NAME OF GAS OR VAPOR
Air	Oxygen	CO_2	H_2O		Air	Oxygen	CO_2	H_2O			Per Cu. Ft.	Per Pound	
4.785	1.0	..	..	CO−2.0	5.771	1.333+	......	....	CO−2.333+	......	......	......	Carbon to CO
9.570	2.0	2.0	..	......	11.541	2.666+	3.666+	....	....	......	......	......	Carbon to CO_2
2.393	0.5	1.0	..	......	2.471	.571	1.571	....	....	......	+138.4	+1809.2	Carbonic oxide
2.393	0.5	..	1.0	......	34.624	8.000	......	9.000	....	......	......	......	Hydrogen
9.570	2.0	1.0	2.0	......	17.312	4.000	2.750	2.250	....	+21,750	+103.1	+2435.6	Methane
16.748	3.5	2.0	3.0	......	16.156	3.733	2.933	1.800	....	+28,560	+136.0	+1713.6	Ethane
23.925	5.0	3.0	4.0	......	15.737	3.636	3.000	1.636	....	+35,110	+167.2	+1436.3	Propane
31.103	6.5	4.0	5.0	......	15.520	3.586	3.034	1.552	....	+42,450	+202.2	+1317.3	Butane
38.280	8.0	5.0	3.0	......	15.386	3.555	3.055	1.500	....	+47,850	+227.9	+1196.2	Pentane
45.458	9.5	6.0	7.0	......	15.205	3.534	3.060	1.465	....	+61,080	+290.0	+1278.4	Hexane
14.355	3.0	2.0	2.0	......	14.836	3.428	3.142	1.286	....	− 2,710	− 12.9	− 174.2	Ethylene
21.533	4.5	3.0	3.0	......	14.836	3.428	3.142	1.286	....	+ 3,220	+ 15.3	+ 138.1	Propylene
28.710	6.0	4.0	4.0	......	14.836	3.428	3.142	1.286	....	+10,660	+ 50.7	+ 342.6	Butylene
35.888	7.5	5.0	5.0	......	14.836	3.428	3.142	1.286	....	+18,970	+113.7	+ 614.1	Amylene
11.963	2.5	2.0	1.0	......	13.313	3.076	3.384	0.692	....	−47,770	−227.5	−3300.7	Acetylene
19.140	4.0	3.0	2.0	......	13.850	3.200	3.300	0.900	....	−39,650	−188.8	−1784.2	Allylene
26.318	5.5	4.0	3.0	......	14.105	3.259	3.259	1.300	....	......	......	......	Crotonylene
35.886	7.5	6.0	3.0	......	13.313	3.076	3.384	0.692	....	−12,510	− 47.3	− 229.3	Benzene
43.065	9.0	7.0	4.0	......	13.547	3.130	3.348	0.782	....	− 3,520	+ 16.7	− 68.8	Toluene
50.243	10.5	8.0	5.0	......	13.720	3.170	3.311	0.849	....	......	......	......	Xylene
57.420	12.0	9.0	6.0	......	13.850	3.200	3.300	0.900	....	+ 490	+ 2.3	+ 7.3	Mesitylene
57.420	12.0	10.0	4.0	......	12.984	3.000	3.437	0.553	....	......	......	......	Naphthalene
7.178	1.5	..	1.0	SO_2−1.0	6.111	1.412	......	0.529	SO_2−1.883	+ 4,740	+ 22.6	+ 250.9	Hydrogen sul.
3.589	0.75	..	1.5	N−0.5	6.111	1.412	......	1.588	N−0.823	+11,890	+ 56.7	+1259.0	Ammonia
5.981	1.25	1.0	0.5	N−0.5	6.410	1.481	1.630	0.333	N−0.518	−27,480	−131.1	−1632.0	Hydrocy. acid
9.570	2.0	2.0	..	N−1.0	5.323	1.230	1.692	....	N−0.538	−65,700	−313.2	−2273.9	Cyanogen
14.355	3.0	1.0	..	SO_2−2.0	5.466	1.263	0.579	....	SO_2−1.684	−26,010	−124.0	− 616.0	Carbon bi-sul.
7.178	1.5	1.0	2.0	......	6.492	1.500	1.375	1.125	....	+51,450	+240.4	+2894.0	Methyl alc.
14.356	3.0	2.0	3.0	......	9.033	2.087	1.913	1.174	....	+58,470	+278.5	+2298.0	Ethyl alcohol
....	..	..	..	......	....	......	......	....	....	......	+463.1	+3979.1	Carbonic acid
....	..	..	..	......	....	......	......	....	....	......	+327.1	+6870.4	Water
....	..	..	..	......	....	......	......	....	....	......	+337.3	+1099.1	Sulfur dioxide
....	..	..	..	......	....	......	......	....	....	......	......	......	Oxygen
....	..	..	..	......	....	......	......	....	....	......	......	......	Nitrogen
....	..	..	..	......	....	......	......	....	....	......	......	......	Air

ODS OF CALCULATION

Columns V and VI are taken chiefly from Lunge's "Coal Tar and Ammonia."

Column VII is from Ganot's "Physics," edition 1896, page 445.

Columns X and XXIII are from Julius Thomsen's "Thermochemical Investigations," and his results are translated into English units in columns XI-XII and XXIV-XXV.

Columns XIII and XVIII are calculated on the assumption that

air = 20.9 % oxygen + 79.1 % nitrogen *by Volume.*

air = 23.13% oxygen + 76.87% nitrogen *by Weight.*

XX.—RELATION OF BAUMÉ DEGREES TO SPECIFIC GRAVITY AND THE WEIGHT OF ONE UNITED STATES GALLON AT 60° F.—LIQUIDS LIGHTER THAN WATER

Baumé.	Specific Gravity.	Pounds in Gallon.	Baumé.	Specific Gravity.	Pounds in Gallon.	Baumé.	Specific Gravity.	Pounds in Gallon.	Baumé.	Specific Gravity.	Pounds in Gallon.
10	1.0000	8.33	31	0.8695	7.24	52	0.7692	6.41	73	0.6896	5.75
11	0.9929	8.27	32	0.8641	7.20	53	0.7650	6.37	74	0.6863	5.52
12	0.9859	8.21	33	0.8588	7.15	54	0.7608	6.34	75	0.6829	5.69
13	0.9790	8.16	34	0.8536	7.11	55	0.7567	6.30	76	0.6796	5.66
14	0.9722	8.10	35	0.8484	7.07	56	0.7526	6.27	77	0.6763	5.63
15	0.9655	8.04	36	0.8433	7.03	57	0.7486	6.24	78	0.6730	5.60
16	0.9589	7.99	37	0.8383	6.98	58	0.7446	6.20	79	0.6698	5.58
17	0.9523	7.93	38	0.8333	6.94	59	0.7407	6.17	80	0.6666	5.55
18	0.9459	7.88	39	0.8284	6.90	60	0.7368	6.14	81	0.6635	5.52
19	0.9395	7.83	40	0.8235	6.86	61	0.7329	6.11	82	0.6604	5.50
20	0.9333	7.78	41	0.8187	6.82	62	0.7290	6.07	83	0.6573	5.48
21	0.9271	7.72	42	0.8139	6.78	63	0.7253	6.04	84	0.6542	5.45
22	0.9210	7.67	43	0.8092	6.74	64	0.7216	6.01	85	0.6511	5.42
23	0.9150	7.62	44	0.8045	6.70	65	0.7179	5.98	86	0.6481	5.40
24	0.9090	7.57	45	0.8000	6.66	66	0.7142	5.95	87	0.6451	5.38
25	0.9032	7.53	46	0.7954	6.63	67	0.7106	5.92	88	0.6422	5.36
26	0.8974	7.48	47	0.7909	6.59	68	0.7070	5.89	89	0.6392	5.33
27	0.8917	7.43	48	0.7865	6.55	69	0.7035	5.86	90	0.6363	5.30
28	0.8860	7.38	49	0.7821	6.52	70	0.7000	5.83	95	0.6222	5.18
29	0.8805	7.34	50	0.7777	6.43	71	0.6965	5.80	..	......	...
30	0.8750	7.29	51	0.7734	6.44	72	0.6930	5.78	..	......	...

XXa.—RELATION OF BAUMÉ DEGREES TO SPECIFIC GRAVITY—LIQUIDS HEAVIER THAN WATER

Baumé Degrees.	Specific Gravity.	Baumé Degrees.	Specific Gravity.	Baumé Degrees.	Specific Gravity.	Baumé Degrees.	Specific Gravity.
0.0	1.0000	6.0	1.0432	24.0	1.1983	42.0	1.4078
0.1	1.0007	7.0	1.0507	25.0	1.2083	43.0	1.4216
0.2	1.0014	8.0	1.0584	26.0	1.2185	44.0	1.4356
0.3	1.0021	9.0	1.0662	27.0	1.2288	45.0	1.4500
0.4	1.0028	10.0	1.0741	28.0	1.2393	46.0	1.4646
0.5	1.0035	11.0	1.0821	29.0	1.2500	47.0	1.4796
0.6	1.0042	12.0	1.0902	30.0	1.2609	48.0	1.4948
0.7	1.0049	13.0	1.0985	31.0	1.2719	49.0	1.5104
0.8	1.0055	14.0	1.1069	32.0	1.2832	50.0	1.5263
0.9	1.0062	15.0	1.1154	33.0	1.2946	51.0	1.5426
1.0	1.0069	16.0	1.1240	34.0	1.3063	52.0	1.5591
1.5	1.0105	17.0	1.1328	35.0	1.3282	53.0	1.5761
2.0	1.0140	18.0	1.1417	36.0	1.3303	54.0	1.5934
2.5	1.0175	19.0	1.1508	37.0	1.3426	55.0	1.6111
3.0	1.0211	20.0	1.1600	38.0	1.3551	56.0	1.6292
3.5	1.0247	21.0	1.1694	39.0	1.3679	57.0	1.6477
4.0	1.0284	22.0	1.1789	40.0	1.3810	58.0	1.6667
5.0	1.0357	23.0	1.1885	41.0	1.3942	59.0	1.6860
						60.0	1.7059

XXI.—COMPARISON OF METRIC AND CUSTOMARY UNITS (U. S.)

Length

1 millimeter, mm.	=0.03937 inch.	1 inch	=25.4001 millimeters.
1 centimeter, cm.	=0.39371 inch.	1 inch	= 2.54001 centimeters.
1 meter, m.	=3.28083 feet.	1 foot	= 0.304801 meter.
1 meter	=1.09361 yards.	1 yard	= 0.914402 meter.
1 kilometer	=0.62137 (U. S.) mile.	1 mile	= 1.60935 kilometers.

Areas

1 square millimeter, sq. mm.	= 0.00155 sq. in.	1 sq. in.	=645.16 sq. mm.
1 square centimeter, sq. cm.	= 0.1550 sq. in.	1 sq. in.	= 6.452 sq. cm.
1 square meter, sq. m.	=10.764 sq. ft.	1 sq. ft.	= 0.0929 sq. m.
1 square meter	= 1.196 sq. yd.	1 sq. yd.	= 0.8361 sq. m.
1 square kilometer	= 0.3861 sq. mi.	1 sq. mi.	= 2.5900 sq. km.
1 hectare	= 2.471 acres.	1 acre	= 0.4047 hectare

Volumes

1 cubic millimeter, cu. mm.	= 0.000061 in.	1 cu. in.	=16,387.2 cu. mm.
1 milliliter, ml.	= 0.06103 cu. in.	1 cu. in.	=16.3872 ml.
1 cubic meter	=35.314 cu. ft.	1 cu. ft.	= 0.02832 cu. m.
	=61,028 cu. ins.		=28.32 liters.
1 cubic meter	= 1.3079 cu. yd.	1 cu. yd.	= 0.7645 cu. m.

Capacities

1 milliliter, ml.	=0.03381 (U. S.) liquid ounce.	1 ounce	=29.574 ml.
1 milliliter	=0.2705 (U. S.) apothecaries' dram.	1 dram	= 3.6967 ml.
1 milliliter	=0.8115 (U. S.) apothecaries' scruple.	1 scruple	= 1.2322 ml.
1 liter	=1.05668 (U. S.) liquid quarts.	1 quart	= 0.94636 liter.
1 liter	=0.26417 (U. S.) gallon.	1 gallon	= 3.78543 liters.
1 liter	=0.11351 (U. S.) peck.	1 peck	= 8.80982 liters.
1 hectoliter	=2.83774 (U. S.) bushels.	1 bushel	= 0.35239 hectoliter.

Masses

1 gram	= 15.4324 grains.	1 grain	= 0.06480 gram.
1 gram	= 0.03527 avoirdupois ounce.	1 ounce (av.)	=28.3495 grams.
1 gram	= 0.03215 troy ounce.	1 ounce (troy)	=31.10348 grams.
1 kilogram	= 2.20462 pounds (av.).	1 pound (av.)	= 0.45359 kilogram.
1 kilogram	= 2.67923 pounds (troy).	1 pound (troy)	= 0.37324 kilogram.

Table of Equivalents, U. S. Bureau of Standards. For British Imperial Weights and Measures see Van Nostrand's Chemical Annual.

Avoirdupois Weight

The system of weights in ordinary use by which common or heavy articles are weighed.

16 drams	=1 ounce	= 28.35 grams.
16 ounces	=1 pound	=453.59 grams.
25 pounds	=1 quarter	= 11.34 kilograms.
4 quarters	=1 hundred weight	= 45.359 kilograms.

1 avoirdupois pound contains 7000 grains.
1 avoirdupois ounce contains 437.5 grains.

Apothecaries' Weight

The system of weights employed in weighing medicines.

1 grain		=	0.0648 gram.
20 grains	= 1 scruple	=	1.296 grams.
3 scruples	= 1 drachm	=	3.888 grams.
8 drachms	= 1 ounce	=	31.103 grams.
12 ounces	= 1 pound	=	373.236 grams.

1 apothecaries' (or troy) pound contains 5760 grains.
1 apothecaries' (or troy) ounce contains 480 grains.

Fluid Measure

1 minim		=	.06161 milliliter.
60 minims	= 1 fluid drachm	=	3.696 milliliters.
8 fluid drachms	= 1 fluid ounce	=	29.573 milliliters.
16 fluid ounces	= 1 pint	=	473.179 milliliters.
8 pints	= 1 gallon	=	3.785 liters.

1 gallon contains 231 cubic inches.

The minim, fluid drachm, fluid ounce and pint are the fluid measures employed by apothecaries.

Other Data

1 cubic foot of water weighs 62.37 pounds.

1 gallon (U. S.) of water weighs 8.33 pounds (the British gallon is 20% more than the U. S.).

1 liter of water weighs approximately 2.2 pounds.

Areas of Plane Figures

Area of any triangle = ½ base multiplied by the altitude.

Rectangle.—Area = base multiplied by altitude, i.e., multiply the length of one side by the length of a perpendicular side.

Parallelogram.—Area = multiply the length of one side by the vertical distance to the parallel side.

Trapezoid.—Area = multiply half the sum of the parallel sides by the perpendicular distance between the two.

Circle.—Area $= 0.7854d^2$, or πr^2 or $\frac{1}{2}Cr$, or $\frac{1}{4}Cd$.
$\pi = 3.1416$, r = radius, C = circumference, d = diameter.

Volumes of Solids

Regular Prism.—Area $= \frac{1}{2}nrah$, or Bh.
n = number of sides, r = perpendicular from center of base to sides of the base, h = height of prism, B = area of base.
Lateral area $= 2\pi rh$.

Right Circular Cylinder.—Volume $= \pi r^2h$ also Bh. Lateral area $= 2\pi rh$.

Regular Pyramid.—Volume = ⅓ altitude multiplied by area of base.

Right Circular Cone.—Volume $= \frac{1}{3}\pi rh$. Lateral area $= \pi rs$.
r = radius of base, s = slant height or $\sqrt{r^2+h^2}$.

Sphere.—Volume $= 4/3\pi r^3$, or $4.189r^3$. Area $= 4\pi r^2$ or $3.1416d^2$.

Barrel or Cask.—Approximate gallons $= .0034n^2h$ where n = mean diameter of barrel. h = height, both measurements in inches.

XXII.—TABLE OF CONSTANTS—GASES*

Name	Formula	Mol. Wt. 0=16, 1930 Atomic Weights	Wt. per Liter in Gms. at 0° C.—760 mm. Hg	Wt. per Cu. Ft. in Lbs., 32° F., 29.92 Hg	Sp.Gr., Air=1
Acetic acid	$C_2H_4O_2$	60.0312	2.678523	.167211	2.072367
Acetone	C_3H_6O	58.0468	2.589987	.161684	2.003867
Acetylene	C_2H_2	26.0156	1.160788	.072464	.898099
Air	—	—	1.292495	.080686	1.000000
Aldehyde	C_2H_4O	44.0312	1.964628	.122645	1.520028
Alcohol, amyl	$C_5H_{11}OH$	88.0936	3.930650	.245377	3.041135
Alcohol, ethyl	C_2H_5OH	46.0468	2.054558	.128259	1.589607
Alcohol, methyl	CH_3OH	32.0312	1.429199	.089220	1.105768
Ammonia	NH_3	17.0314	.759917	.047439	.587946
Aniline	$C_6H_5NH_2$	93.0626	4.152351	.259217	3.212664
Argon	Ar	39.9400	1.782078	.111249	1.378789
Arsine (Hydrogen arsenide)	AsH_3	77.9534	3.478199	.217132	2.691074
Benzene	C_6H_6	78.0468	3.482364	.217392	2.694296
Boron chloride	BCl_3	117.1910	5.228944	.326425	4.045621
Boron fluoride	BF_3	67.8200	3.026051	.188906	2.341249
Bromine	Br_2	159.8320	7.131531	.445197	5.517649
Butane	C_4H_{10}	58.0780	2.591381	.161771	2.004945
Carbon bisulfide	CS_2	76.1300	3.396391	.212025	2.627779
Carbon dioxide	CO_2	44.0000	1.963235	.122558	1.518950
Carbon monoxide	CO	28.0000	1.249324	.077991	.966599
Carbon tetrachloride	CCl_4	153.8280	6.863648	.428474	5.310388
Carbonyl chloride	$COCl_2$	98.9140	4.413441	.275516	3.414669
Carbonyl sulfide	COS	60.0600	2.679821	.167292	2.073371
Cyanogen	C_2N_2	52.0160	2.320903	.144886	1.795677
Chlorine	Cl_2	70.9140	3.164102	.197524	2.448058
Chlorine dioxide	ClO_2	67.4570	3.009856	.187895	2.328719
Chlorine monoxide	Cl_2O	86.9140	3.878012	.242091	3.000409
Chlorosulfonic acid	SO_3HCl	116.5248	5.199213	.324569	4.022619
Ethane	C_2H_6	30.0468	1.340663	.083693	1.037268
Ethyl chloride	C_2H_5Cl	64.4960	2.877749	.179648	2.226508
Ethyl fluoride	C_2H_5F	48.0390	2.143446	.133808	1.658379
Ethylene	C_2H_4	28.0312	1.250718	.078078	.967677
Fluorine	F_2	38.0000	1.695528	.105846	1.311826
Fluosulfonic acid	SO_3HF	100.0678	4.464926	.278730	3.454503
Helium	He	4.0020	.178562	.011147	.137905
Hydrobromic acid	HBr	80.9238	3.610738	.225406	2.793620
Hydrochloric acid	HCl	36.4648	1.627016	.101569	1.258818
Hydrocyanic acid	HCN	27.0158	1.205416	.075250	.932628
Hydrofluoric acid	HF	20.0078	.892729	.055730	.690702

* Calculated by T. C. Cummings, General Chemical Co.

NOTE.—International Critical Tables, 22.412 liters = molecular weight in gms.

XXII.—TABLE OF CONSTANTS—GASES (*Continued*)

Name	Formula	Mol. Wt. O = 16, 1930 Atomic Weights	Wt. per Liter in Gms. at 0° C.—760 mm. Hg	Wt. per Cu. Ft. in Lbs., 32° F., 29.92 Hg	Sp.Gr., Air = 1
Hydrofluosilicic acid	H_2SiF_6	144.0756	6.428497	.401309	4.973713
Hydriodic acid	HI	127.9398	5.708547	.356365	4.416689
Hydrogen	H_2	•2.0156	.089930	.005614	.069578
Hydrogen selenide	H_2Se	81.2156	3.623762	.226219	2.806396
Hydrogen sulfide	H_2S	34.0756	1.520410	.094914	1.176338
Hydrogen telluride	H_2Te	129.5156	5.778854	.360754	4.471085
Iodine	I_2	253.8640	11.327149	.707115	8.763788
Krypton	Kr	82.9000	3.698906	.230910	2.861835
Methane	CH_4	16.0312	.715288	.044653	.553417
Methyl chloride	CH_3Cl	50.4804	2.252390	.140609	1.742669
Methyl fluoride	CH_3F	34.0234	1.518088	.094769	1.174541
Mercury	Hg	200.6100	8.951013	.558781	6.925377
Neon	Ne	20.1830	.900546	.056218	.696750
Nitrogen	N_2	28.0160	1.250045	.078036	.967157
Nitrogen (Atmospheric)	—	—	1.256821	.078459	.972399
Nitrogen dioxide	NO_2	46.0080	2.052828	.128151	1.588268
Nitrogen pentoxide	N_2O_5	108.0160	4.819567	.300869	3.728887
Nitrogen tetroxide	N_2O_4	92.0160	4.105656	.256302	3.176536
Nitrogen trioxide	N_2O_3	76.0160	3.391761	.211736	2.624198
Nitrosyl chloride	NOCl	65.4650	2.920984	.182347	2.259958
Nitrous oxide	N_2O	44.0160	1.963956	.122603	1.519508
Nitric oxide	NO	30.0080	.858369	.083585	1.035929
Nitric acid	HNO_3	63.0158	2.811704	.175525	2.175408
Oxygen	O_2	32.0000	1.427806	.089133	1.104690
Ozone	O_3	48.0000	2.141716	.133700	1.657041
Pentane	C_5H_{12}	72.0936	3.216739	.200810	2.488784
Phosphine (Hydrogen phosphide)	PH_3	34.0434	1.518985	.094825	1.175235
Phosphorus	P_4	124.0800	5.536313	.345613	4.283432
Propane	C_3H_8	44.0624	1.966022	.122732	1.521107
Propylene	C_3H_6	42.0468	1.876076	.117117	1.451516
Silicon fluoride	SiF_4	104.0600	4.643055	.289850	3.592321
Stibine (Hydrogen antimonide)	SbH_3	124.7800	5.568158	.347601	4.308071
Sulfur	S_2	64.1200	2.860961	.178600	2.213519
Sulfur	S_8	256.4800	11.443862	.714401	8.854089
Sulfur dioxide	SO_2	64.0600	2.858286	.178433	2.211449
Sulfur trioxide	SO_3	80.0600	3.572197	.223000	2.763800
Water	H_2O	18.0156	.803840	.050181	.621929
Xenon	Xe	130.2000	5.809386	.362660	4.494708

USEFUL MEMORANDA

GAS CALCULATIONS

Conversion Formulae for Gas Volumes.—Conversion from existing to standard conditions,

$$V=\frac{V'\times 273\times(P-w)}{(273+t)\times 760}.$$

Gas at standard volume to new conditions of temperature and pressure

$$V'=\frac{V\times(273+t)\times 760}{273\times(P-w)}$$

V = standard volume, V' = volume under other conditions of temperature and pressure (other than 0° C. and 760 mm. Hg pressure).

t = temperature of the gas, P = barometric pressure in mm. Hg + static pressure of the gas. w = water vapor pressure at temperature and pressure that the gas is measured or to which it is to be converted.

Pitot Formulae for Measuring the Velocity of a Gas in a Flue.—

A. Simple formula for fair approximations $V=42\sqrt{h}$.

B. More exact formula $V=1290\dfrac{\sqrt{\tfrac{1}{2}h(1+.00217t)}}{BM}$.

V = velocity in feet per second. h = gauge reading in terms of water, i.e., the total differential in terms of vertical reading. In a gauge inclined 1 : 10, with ether in place of water, 10″ differential $=10\times.72\div10=.72$. In the formula *B* ½ the reading is taken as the deflection due to velocity pressure is half the total deflection (proven by repeated tests, suction is produced by the gas flow on the straight petot arm). Allowance is made for this in formula *A*. t = temperature of the gas measured. B = barometric pressure + plus static pressure of the gas in terms of inches of mercury (air standard 29.92″). M = specific gravity of the gas compared with the hydrogen molecule $H_2=2.016$.

To obtain the specific gravity of a gas, multiply the molecular weight of each constituent by its per cent ratio in the mixture, divide by 100 and finally divide the sum of these results by 2.016.

Examples.—The sp.gr. of a gas having the composition 87% nitrogen, 5% oxygen, and 8% sulfur dioxide we would find

$$\begin{aligned}&28.02(N_2)\times 87\div 100=24.38\\&32.00(O_2)\times 5\div 100=1.6\\&64.06(SO_2)\times 8\div 100=5.12\ \text{total}=31.1\ \text{sp.gr.}=\frac{31.1}{2.016}=15.42.\end{aligned}$$

The sp.gr. of air containing 78% nitrogen, 21% oxygen, 1% argon would be

$$\begin{aligned}&28.02\times.78=21.86,\\&32.00\times.21=6.72,\\&39.88\times.1=0.4\quad \text{total}=28.98\ \text{sp.gr.}=14.38.\end{aligned}$$

Consult table XXII.

The gram molecular weight of any gas occupies 22.4 liters.

DEFINITIONS

Heat

Calorie is 1/100 of the heat required to raise the temperature of one gram of water from 0° C. to 100° C.

One kilogram calorie = 1000 gram calories or 3.968 B.t.u.

Latent heat of evaporation is the quantity of heat required to convert 1 gram of a liquid into vapor without change of temperature.

Latent heat of fusion is the quantity of heat required to change a gram of the substance from a solid to a liquid state without changing temperature.

Specific Heat.—The British thermal unit (B.t.u.) = 1/180 part of the heat required to raise the temperature of one pound of water from 32° F. to 212° F.

Specific heat of a body is the quantity of heat required to raise the temperature of a unit weight of that body 1° C.

Photometry

Lux.—This is the practical unit of illumination and is the light received from a source of 1 meter distance.

Foot-candle.—This is the illumination received by a standard candle at one foot distance. The candle loses in burning 120 grams per hour.

1 foot-candle = 10.76 lux.

Candle-power.—The comparison of the illumination of a light with one standard candle. A simple method for determination is to place the light and the burning candle 60 inches apart (2 meters and 100 inches distance also taken). A screen with a spot of oil is so placed between the lights as to receive a uniform illumination on each side, which is readily seen by the spot. The square of the distance from the screen to the light tested divided by the square of the distance from the screen to the standard candle = the candle-power of the light. When gas is tested the flame is so regulated that it burns 5 cubic feet of gas an hour. The standard candle burns 120 grams per hour as stated above.

Units in Electricity

Ampere is the unit of current flow. An ampere will deposit from a silver nitrate solution 1.118 milligrams of silver (.001118 g.) per second.

Coulomb is the unit of quantity. One coulomb will deposit .001118 g. Ag (time factor not considered as in case of ampere). 96,494 coulombs will deposit the gram equivalent of an element from a solution of its salt, i.e., 107.88 grams of silver, $\frac{63.57}{2}$ grams of cupric copper Cu^{++}, $\frac{55.84}{3}$ of ferric iron Fe^{+++}, 63.57 of cuprous copper Cu^{+}, $\frac{55.84}{2}$ gram of ferrous iron Fe^{++}, etc. One gram equivalent of an element carries 96,500 (round numbers) coulombs.

Electromotive force—E.M.F.—is the force causing electricity to move.

Other Terms

Erg.—This is the unit of work and is that work done by a force of 1 dyne when it acts through a distance of 1 cm.

Dyne = the force which acting on one gram for one second produces a velocity of one centimeter per second.

Joule.—This is the practical unit of electrical energy and is produced when a steady current of one coulomb per second, i.e., one ampere, passes through a resistance of one ohm for one second.

Ohm.—This is the resistance that is offered at 0° C. by a column of mercury 106.3 centimeters long, being 1 square millimeter in cross section and weighing 14.4521 grams.

Volt.—This is the electromotive force which produces one ampere of current through a conductor having a resistance of one ohm.

If any two of the factors are known the third can be found by the formula $I = E/R$; I = ampere current, E = electromotive force (volts) and R = ohms resistance.

Watt.—One watt is produced when one ampere of current flows under a pressure of one volt (E.M.F.).

One watt = .00134 horse power, = 44.25 foot pounds, per minute, = 14.33 gram calories per minute, = .057 B.t.u. per minute.

Watt-hour and kilowatt-hour are the units of energy used in commercial electrical work.

Watt-hour = 3600 joules, = 2655.4 ft. lbs., = 859975 gram calories, = 3.412 B.t.u. = .001341 h.p. hr.

One kilowatt = 1000 watts.

Foot-pound is the unit of work done in raising a weight of one pound through a distance of one foot. Work = weight multiplied by height, or force multiplied by distance.

Horse power = 550 foot pounds.

Specific gravity of a substance is the ratio of the weight of a given volume of that substance compared with the weight of an equal volume of water.

a. Solid heavier than water. Weight of solid in the air divided by the difference between this weight and its weight in water = sp.gr. of solid.

b. Solid lighter than water. The weight of the solid in the air divided by this weight + the loss of weight of a sinker due to the buoyancy of the solid = sp.gr.

c. Solid soluble in water. Determine gravity in a liquid in which it is insoluble whose specific gravity is known, multiply the gravity in terms of the liquid by the gravity of the liquid = sp.gr. in terms of water.

d. Liquids. Compare with water by weighing in a specific gravity bottle; the bottle being filled with water is weighed, the bottle, drained and dried, is filled with the liquid and again weighed; the weights are compared on subtracting the weight of the empty bottle.

e. The loss of weight of an insoluble substance immersed in the liquid is divided by the loss of weight of the substance immersed in water = sp.gr.

f. The specific gravity is determined by the hydrometer. See chapter on Acids, Volume II.

VOLUME AND WEIGHT CONVERSION TABLE

To Convert From	Multiply by To Cu. In.	To Cu. Ft.	To Cu. Yd.	To Fl. Oz.	To Pint.	To Quart.	To Gallon.	To Grain.	To Oz. Troy	To Oz. Av.	To Lb. Troy.	To Lb. Av.	To Ml. or G.	To Ltr. or Kg.	To Cu. M.
Cu. In. . .	1.00000	$.0_{3}5787$	$.0_{4}2143$	.554112	.034632	.017316	.004329	252.891	.526857	.578037	.043905	.036127	16.3871	.016387	$.0_{4}1639$
Cu. Ft. . .	1728.00	1.00000	.037037	957.505	59.8442	29.9221	7.48052	436996	910.408	998.848	75.8674	62.4280	28316.9	28.3169	.028317
Cu. Yd. .	46656.0	27.0000	1.00000	25852.6	1615.79	807.896	201.974	117990_{3}	24581.0	26968.9	2048.42	1685.56	764556	764.556	.764556
Fl. Oz. . .	1.80469	.001044	$.0_{4}3868$	1.00000	.062500	.031520	.007813	456.390	.950813	1.04318	.079234	.065199	29.5736	.029573	$.0_{4}2957$
Pint.	28.8750	.016710	$.0_{3}6189$	16.0000	1.00000	.500000	.125000	7302.23	15.2130	16.6908	1.26775	1.04318	473.177	.473177	$.0_{3}4732$
Quart . . .	57.7500	.033420	.001238	32.0000	2.00000	1.00000	.250000	1460.45	30.4260	33.3816	2.53550	2.08635	946.354	.946354	$.0_{3}9463$
Gallon . . .	231.000	.133681	.004951	128.000	8.00000	4.00000	1.00000	58417.9	121.704	133.527	10.1420	8.34541	3785.42	3.78542	.003785
Grain . . .	.003954	$.0_{5}2288$	$.0_{7}8475$	.002191	$.0_{3}1369$	$.0_{4}6850$	$.0_{4}1712$	1.00000	.002083	.002286	$.0_{3}1736$	$.0_{3}1428$	.064799	$.0_{4}6479$	$.0_{7}6479$
Oz. Troy	1.89805	.001098	$.0_{4}4068$	1.05173	.065733	.032867	.008217	480.000	1.00000	1.09714	.083333	.068571	31.1035	.031104	$.0_{4}3110$
Oz. Av. . .	1.72999	.001001	$.0_{4}3708$	.958608	.059913	.029957	.007489	437.500	.911457	1.00000	.075955	.062500	28.3495	.028350	$.0_{4}2835$
Lb. Troy	22.7766	.013181	$.0_{3}4882$	12.6208	.788800	.394400	.098600	5760.00	12.0000	13.1657	1.00000	.822857	373.242	.373242	$.0_{3}3732$
Lb. Av. .	27.6799	.016018	$.0_{3}5933$	15.3378	.958611	.479306	.119826	70000.0	14.5833	16.0000	1.21528	1.00000	453.593	.453593	$.0_{3}4536$
Ml. or Gram .	.061024	$.0_{4}3531$	$.0_{5}1308$	.033814	.002113	.001057	$.0_{3}2642$	15.4323	.032151	.035274	.002679	.002205	1.00000	.001000	.000001
Liter or Kg. . . .	61.0237	.035315	.001308	33.8140	2.11337	1.05669	.264172	15432.3	32.1507	35.2739	2.67923	2.20462	1000.00	1.00000	.001000
Cu. M. . .	61023.7	35.3146	1.30795	33814.0	2113.37	1056.69	264.172	154320_{3}	32150.7	35273.9	2679.23	2204.62	1000000	1000.00	1.00000

Note. The small subnumeral following a zero indicates that the zero is to be taken that number of times: thus, $.0_{3}1428$ is equivalent to .0001428.

Values used in constructing table:

1 inch = 2.540001 cm.

∴ 1 cu. in. = 16.387083 cc. = 16.387083 g H_2O at 4°C = 39°F.

231 cu. in. = 1 gallon = 3785.4162 g.

1 lb. av. = 453.5926 g.

∴ 1 gal. = 8.34541 lb.

∴ 1 lb. av. = 27.679886 cu. in. H_2O at 4°C.

1 lb. av. = 7000 grains

∴ 1 gallon = 58417.87 grains

ENERGY CONVERSION FACTORS

To Convert From	Multiply by										
	B. T. U.	P. C. U.	Cal.	Ft. Lbs.	Ft. Tons	Kg. M.	HP Hrs.	KW Hrs.	Joules	Lbs. C	Lbs. H_2O
B. T. U.	1.00000	.555556	.251996	778.000	.389001	107.563	$.0_{3}3929$	$.0_{3}2931$	1055.20	$.0_{4}6876$	.001031
P. C. U.	1.80000	1.00000	.453593	1400.40	.700202	193.613	$.0_{3}7072$	$.0_{3}5276$	1899.36	$.0_{3}1238$	.001855
Calories	3.96832	2.20462	1.00000	3091.36	1.54368	426.844	.001559	.001163	4187.37	$.0_{3}2729$	.004089
Ft. Lbs.	.001285	$.0_{3}7141$	$.0_{3}3239$	1.00000	.000500	.138255	$.0_{6}5050$	$.0_{6}3767$	1.35625	$.0_{7}8840$	$.0_{5}1325$
Fr. Tons	2.57069	1.42816	.647804	2000.00	1.00000	276.511	.001010	$.0_{3}7535$	2712.59	$.0_{3}1768$	.002649
Kg. M.	.009297	.005165	.002343	7.23301	.003617	1.00000	$.0_{5}3653$	$.0_{5}2725$	9.81009	$.0_{6}6394$	$.0_{5}9580$
HP Hrs.	2544.99	.141388	641.327	1980000	990.004	273747	1.00000	.746000	2685473	.175044	2.62261
KW Hrs.	3411.57	1895.32	859.702	2654200	1327.10	366959	1.34041	1.00000	3599889	.234648	3.51562
Joules	$.0_{3}9477$	$.0_{3}5265$	$.0_{3}2388$	.737311	$.0_{3}3687$	.101937	$.0_{6}3724$	$.0_{6}2778$	1.00000	$.0_{7}6518$	$.0_{6}9766$
Lbs. C.	14544.0	8080.00	3665.03	113150_{3}	5657.63	1564396	5.71434	4.26285	153470_{3}	1.00000	14.9876
Lbs. H_2O	970.400	539.111	244.537	754971	377.487	104379	.381270	.284424	1023966	.066744	1.00000

"P. C. U." refers to the "pound-centigrade unit." The ton used is 2000 pounds. "Lbs. C" refers to pounds of carbon oxidized, 100 % efficiency, equivalent to the corresponding number of heat units. "Lbs. H_2O" refers to pounds of water evaporated at 100° C. = 212° F. at 100% efficiency. The sub-numeral following a zero indicates that the zero should be taken the number of times indicated. Thus: $0_{5}3653$ is equivalent to .000003653.

INTER-CONVERSION TABLE

To Convert from	Multiply by									
	Grains per Cu. Ft.	Ounces per Cu. Ft.	Pounds per Cu. Ft.	Grams per Cu. Ft.	Grains per Gallon	Ounces per Gallon	Pounds per Gallon	Grains per Cu. In.	Ounces per Cu. In.	Grams per Liter
Grains per Cu. Ft.	1.00000	.002286	$.0_{3}1428$	.064799	.133680	$.0_{3}3056$	$.0_{4}1910$	$.0_{3}5787$	$.0_{5}1323$	.002288
Oz. per Cu. Ft.	437.500	1.00000	.062497	28.4954	58.4848	.133678	.008355	.253180	$.0_{3}5786$	1.00103
Lbs. per Cu. Ft.	7000.00	16.0000	1.00000	453.593	935.757	2.13885	.133680	4.05090	.009258	16.0163
G. per Cu. Ft.	15.4324	.035274	.002205	1.00000	2.06302	.004715	$.0_{3}2947$	.008931	$.0_{4}2041$	.035310
Grains per Gallon	7.48050	.017098	.001069	.484727	1.00000	.002286	$.0_{3}1428$	.004329	$.0_{5}9894$	.017116
Oz. per Gallon	3272.72	7.48050	.467510	21.2068	437.500	1.00000	.062499	1.89392	.003429	7.48798
Lbs. per Gallon	52363.6	119.690	7.48014	3393.09	7000.00	16.0000	1.00000	30.3028	.069261	119.808
Grains per Cu. In.	1728.00	3.94960	.246840	111.972	231.000	.527990	.032990	1.00000	.002285	3.95380
Oz. per Cu. In.	756000	1728.00	108.000	48987.8	101061	231.000	14.4370	437.500	1.00000	1729.73
G. per Liter	437.050	.998950	.062432	28.3203	58.4220	.133540	.008346	.252910	$.0_{3}5780$	1.00000

INTER-CONVERSION TABLE

To Convert From	Multiply by				
	Lbs. per Sq. In.	Tons per Sq. In.	Kg. per Sq. Cm.	M. Tons per Sq. Cm.	Atmospheres
Lbs. per Sq. In....	1.00000	.000446	.070307	$.0_47031$	.068041
Tons per Sq. In...	2240.00	1.00000	157.488	.157488	152.412
Kg. per Sq. Cm....	14.2233	.006350	1.00000	.001000	.967768
Metric Tons per Sq. Cm.........	14223.0	6.34969	1000.00	1.00000	967.768
Atmospheres......	14.6970	.006558	1.03329	.001033	1.00000

1 gram = 15.43 grams

1 gram = .0408 grams

1 m. = 3.28 ft.

The above tables were obtained by courtesy of E. I. DuPont de Nemours and Company through the kindness of Dr. E. C. Lathrop.

log 12 = 1.0792
colog 12 = 8.9208-10

log 144 = 2.1584
colog 144 = 7.8416-10

No.	0	1	2	3	4	5	6	7	8	9	PP 1	PP 2	PP 3	PP 4	PP 5	PP 6	PP 7	PP 8	PP 9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

$\pi = 3.1416$

log π = 0.4971
colog π = 9.5029-10

COMPUTED BY H. G. SHAW, PH.D.

A convenient chart mounted on cardboard may be obtained of the above logarithms and the following antilogarithms from L. E. Knott Apparatus Co., 79–83 Amherst Street, Cambridge, Mass.

log 60 = 1.7782 log .55 = 9.7404-10
colog 60 = 8.2218-10 colog .55 = 0.2596

No.	0	1	2	3	4	5	6	7	8	9	PP 1	PP 2	PP 3	PP 4	PP 5	PP 6	PP 7	PP 8	PP 9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

g = 32.16 log g = 1.5073
colog g = 8.4927-10

Mant.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
											PROPORTIONAL PARTS.								
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	3	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

Log.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
											PROPORTIONAL PARTS.								
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

COMMON MINERALS

			Specific Gravity
Aluminum	Al		2.60
Andalusite	Al_2SiO_5	Silicate of aluminum	3.16– 3.20
Anglesite	$PbSO_4$	Lead sulfate	6.12– 6.39
Anthracite		Hard Coal	1.32– 1.70
Antimony	Sb		6.71
Apatite	$3Ca_3P_2O_8, CaF_2$	Phosphate of lime	3.17– 3.23
Aragonite	$CaCO_3$	Carbonate of lime	2.94
Argentite	Ag_2S	Silver sulfide	7.20– 7.36
Arsenic	As		5.73
Arsenolite	As_2O_3	White arsenic	3.70– 3.72
Asphaltum			1.0 – 1.80
Atacamite	$CuCl_2 \cdot 3Cu(OH)_2$	Chloride of copper	3.75
Azurite	$Cu_3(OH)_2(CO_3)_2$	Blue carbonate of copper	3.77– 3.83
Barite	$BaSO_4$	Barium sulfate	4.3 – 4.6
Bauxite	$Al_2O_3 \cdot 2H_2O$	Hydrate oxide of aluminum	2.55
Beryl	$Be_3Al_2Si_6O_{18}$	Silicate of beryllium	2.63– 2.80
Biotite		Magnesia-iron mica	2.70– 3.10
Bismuth	Bi		9.80
Bismuthinite	Bi_2S_3	Sulfide of bismuth	6.4 – 6.50
Bituminous Coal		Soft Coal	1.14– 1.40
Bornite	Cu_3FeS_3	Sulfide of copper and iron	4.90– 5.40
Cadmium	Cd		8.60
Calamine	$H_2Zn_2SiO_5$	Silicate of zinc	3.40– 3.50
Calcite	$CaCO_3$	Carbonate of lime	2.7
Cassiterite	SnO_2	Dioxide of tin	6.8 – 7.10
Cerargyrite	AgCl	Horn silver	5.55
Cerussite	$PbCO_3$	Carbonate of lead	6.46– 6.57
Chalcocite	Cu_2S	Copper glance	5.5 – 5.8
Chalcopyrite	$CuFeS_2$	Copper pyrite	4.1 – 4.3
Chromite	$FeCr_2O_4$	Chromic iron	4.32– 4.57
Chromium	Cr		6.50
Chrysolite	$(MgFe)_2SiO_4$	Silicate of magnesia and iron	3.27– 3.37
Cinnabar	HgS	Sulfide of mercury	8.0 – 8.2
Cobalt			8.6
Cobaltite	CoAsS	Sulf-arsenide of cobalt	6.0 – 6.30
Copper	Cu		8.8 – 8.90
Corundum	Al_2O_3	Oxide of aluminum	3.95– 4.10
Cryolite	Na_3AlF_6	Fluoride of aluminum and sodium	3.00
Cuprite	Cu_2O	Red copper ore	5.85– 6.15
Cyanite	Al_2SiO_5	Aluminum silicate	3.56– 3.67
Diamond	C		3.50
Dolomite	$(CaMg)CO_3$	Carbonate of lime and magnesia	2.80– 2.90
Enargite	$CuAsS_4$		4.45
Epidote	$HCa_2(AlFe)_3Si_3O_{13}$	Silicate of iron alumina and lime	3.25– 3.5
Fluorite	CaF_2	Fluor spar	3.2
Franklinite		Oxide of zinc, manganese and iron	5.07– 5.22
Galena	PbS	Sulfide of lead	7.43
Garnet			3.15– 4.3
Gold	Au		15.6 –19.3
Graphite	C		2.09– 2.23
Gypsum	$CaSO_4+2H_2O$	Sulfate of lime	2.3
Hematite	Fe_2O_3	Red oxide of iron	4.9 – 5.3
Ice	H_2O		0.916
Iodyrite	AgI	Iodide of silver	5.6 – 5.7
Iridium	Ir		22.42
Iron	Fe		7.86

COMMON MINERALS—*Continued*

Mineral	Formula	Description	Specific Gravity
Kaolinite	$2H_2O \cdot Al_2O_3 \cdot 2SiO_2$	Silicate of alumina	2.6
Lead	Pb		11.37
Limonite	$2Fe_2O_3 \cdot 3H_2O$	Brown oxide of iron	3.6 – 4.0
Magnesite	$MgCO_3$	Carbonate of magnesia	3.0 – 3.12
Magnetite	FeO, Fe_2O_3	Magnetic oxide of iron	5.16– 5.18
Malachite	$Cu_2(OH)_2CO_3$	Green carbonate of copper	3.9 – 4.0
Manganese	Mn		7.39
Manganite	$Mn_2O_3 \cdot H_2O$	Hydrated manganese oxide	4.2 – 4.4
Monazite			4.8 – 5.1
Marcasite	FeS_2	White iron pyrite	4.85– 4.90
Mercury	Hg		13.6
Millerite	NiS	Nickel sulfide	5.3 – 5.6
Mimetite	$3PB_3As_2O_8PbCl_2$	Lead arsenate	7.0 – 7.25
Muscovite	$H_2KAl_3(SiO_4)_3$	Potash mica	2.76– 3.0
Naphtha			0.60– 0.756
Niccolite	NiAs	Nickel arsenide	7.33– 7.67
Nickel	Ni		8.9
Opal	$SiO_2 \cdot nH_2O$		1.9 – 2.3
Orpiment	As_2S_3	Yellow sulfide of arsenic	3.4 – 3.5
•Orthoclase	$KAlSi_3O_8$	Potash feldspar	2.46– 2.6
Ozocerite		Mineral wax	0.85– 0.90
Palladium	Pd		11.3 –11.8
Platinum	Pt		14.0 –19.0
Proustite	Ag_3AsS_3	Light red silver ore	5.57– 5.64
Pyrargyrite	Ag_3SbS_3	Dark red silver ore	5.77– 5.86
Pyrite	FeS_2	Iron sulfide	4.95– 5.10
Pyrolusite	MnO_2	Dioxide of manganese	4.82
Pyromorphite	$3Pb_3P_2O_8PbCl_2$	Lead phosphate	6.5 – 7.1
Pyrrhotite	$Fe_{11}S_{12}$	Magnetic pyrite	4.58– 4.64
Quartz	SiO_2		2.65– 2.66
Realgar	AsS	Red sulfide of arsenic	3.55
Rhodochrosite	$MnCO_3$	Carbonate of manganese	3.45– 3.6
Rhodonite	$MnSiO_3$	Silicate of manganese	3.40– 3.68
Rutile	TiO_2	Dioxide of titanium	4.2
Serpentine	$H_4Mg_3Si_2O_9$	Silicate of magnesia	2.50– 2.65
Siderite	$FeCO_3$	Carbonate of iron	3.8 – 3.9
Silver	Ag		10.1 –11.1
Smaltite	$CoAs_2$	Arsenide of cobalt	6.4 – 6.6
Smithsonite	$ZnCO_3$	Carbonate of zinc	4.30– 4.45
Sphalerite	ZnS	Sulfide of zinc	3.9 – 4.
Spinel	$MgAl_2O_4$	Aluminate of magnesia	3.5 – 4.1
Stephanite	Ag_5SbS_4	Brittle silver	6.2 – 6.3
Stibnite	Sb_2S_3	Sulfide of antimony	4.5 – 4.6
Sulfur	S		2.08
Sylvanite	(Au, Ag)Te	Telluride of gold and silver	7.9 – 8.3
Talc	$H_2Mg_3Si_4O_{12}$	Silicate of magnesia	2.7 – 2.8
Tephroite	Mn_2SiO_4	Silicate of manganese	4.0 – 4.1
Tetrahedrite	$4Cu_2S$, Sb_2S_3	Gray copper	4.4 – 5.1
Tin	Sn		7.29
Topaz		Fluo-silicate of alumina	3.4 – 3.6
Tourmaline		Silicate of alumina, iron and magnesia	2.98– 3.20
Willemite	Zn_2SiO_4	Silicate of zinc	3.9 – 4.18
Wolframite	(Fe, Mn)WO_4	Tungstate of iron and manganese	7.2 – 7.5
Wulfenite	$PbMoO_4$	Molybdate of lead	6.7 – 7.0
Zinc	Zn		7.15
Zincite	ZnO	Zinc oxide	5.43– 5.7
Zircon	$ZrSiO_4$	Silicate of zirconium	4.70

HEAT OF COMBUSTION

COMPILED BY N. F. WILSON, JR.

Lefax

Heat of Combustion of Various Materials

Material	Burned to	Heat Produced		Authority
		Calories per Gm.	B.T.U. per Lb.	
Alcohol, ethyl	CO_2+H_2O liquid	7,183	12,931	Favre & Silberman
Alcohol, ethyl	CO_2+H_2O liquid	6,850	12,530	Andrews
Alcohol, methyl		5,322	9,579	Anonymous
Alcohol, amyl	CO_2+H_2O liquid	8,933	16,079	Anonymous
Antimony	Sb_2O_4	961	1,730	Dulong
Asphalt		9,532	17,159	Slossen & Colburn
Benzol, C_6H_6 gas	CO_2+H_2O liquid	10,070	18,126	Berthelot
Benzol, C_6H_6 gas	CO_2+H_2O liquid	9,650	17,370	Anonymous
Benzol, C_6H_6 liquid	CO_2+H_2O liquid	10,030	18,054	Stohman
Cane sugar		3,961	7,130	Berthelot
Carbon, bisulfide	CO_2	3,401	6,122	Favre & Silberman
Carbon, crystallized	CO	2,405	4,329	Berthelot
Carbon, crystallized	CO_2	7,859	14,146	Berthelot
Carbon, amorphous	CO	2,489	4,480	Berthelot
Carbon, amorphous	CO_2	8,137	14,647	Berthelot
Carbon, amorphous	CO_2	8,080	14,544	Berthelot
Carbon, vapor	CO_2	11,328	20,390	Berthelot
Carbon, vapor diamond	CO_2	11,134	20,041	Berthelot
Carbonic, oxide CO	CO_2	5,640	10,152	Thomsen
Cellulose	CO_2+H_2O liquid	4,208	7,574	Berthelot
Charcoal	CO	2,473	4,451	Favre & Silberman
Charcoal	CO	2,442	4,396	Berthelot
Charcoal	CO_2	8,080	14,544	Favre & Silberman
Charcoal	CO_2	8,137	14,647	Berthelot
Charcoal, beech	CO_2	7,140	12,852	Schwackhöfer
Charcoal, soft	CO_2	7,071	12,723	Schwackhöfer
Charcoal, sugar	CO_2	8,040	14,472	Favre & Silberman
Coal, anthracite		7,800	14,040	Various
Coal, bituminous		8,500	15,300	Average of various
Coal, coke		7,000	12,600	Average of various
Coal, lignite		6,900	12,420	Average of various
Cyanogen	CuO	5,195	9,351	Dulong
Coke, gas	CO_2	8,047	14,485	Favre & Silberman
Coke, petroleum	CO_2	8,017	14,430	Mohler
Copper	CuO	590	1,062	Thomsen
Dynamite, 75%		1,290	2,322	Roux & Sarran
Gas, acetylene C_2H_2	CO_2+H_2O liquid	12,142	21,855	Berthelot
Gas, acetylene C_2H_2	CO_2+H_2O liquid	11,527	20,749	Thomsen
Gas, coal		4,440	7,990	Anonymous
Gas, coal		7,370	12,266	Anonymous
Gas, ethylene C_2H_4	CO_2+H_2O liquid	11,858	21,344	Favre & Silberman
Gas, ethylene C_2H_4	CO_2+H_2O liquid	12,072	21,730	Berthelot
Gas, ethylene C_2H_4	CO_2+H_2O gas	11,293	20,327	Berthelot
Gas, methane CH_4	CO_2+H_2O liquid	13,063	23,513	Favre & Silberman
Gas, methane CH_4	CO_2+H_2O liquid	13,344	24,019	Berthelot
Gas, methane CH_4	CO_2+H_2O gas	12,066	21,719	Berthelot
Gas, petroleum		10,800	19,440	Anonymous
Gas, producer		773	1,391	Anonymous
Gas, producer		1,370	2,466	Anonymous

Material	Burned to	Heat Produced		Authority
		Calories per Gm.	B.T.U. per Lb.	
Gas, naphthalene	CO_2+H_2O liquid	9,793	17,637	Anonymous
Gas, naphthalene	CO_2+H_2O liquid	9,690	17,442	Berthelot
Gas, naphthalene	CO_2+H_2O gas	9,354	16,837	Berthelot
Gas, water		2,350	4,230	Anonymous
Gas, water		3,032	5,458	Anonymous
Glycerin	CO_2+H_2O liquid	4,316	7,769	Stohman
Graphite	CO_2	7,901	14,222	Berthelot
Gunpowder		750	1,350	Various
Hydrogen	H_2O liquid	34,462	62,032	Favre & Silberman
Hydrogen	H_2O liquid	34,180	61,524	Thomsen
Hydrogen	H_2O liquid	34,500	62,100	Berthelot
Hydrogen	H_2O gas	28,800	51,840	Thomsen
Hydrogen	H_2O gas	29,150	52,470	Berthelot
Iron	Fe_3O_4	1,702	3,064	Dulong
Iron	Fe_2O_3	1,582	2,848	Anonymous
Magnesium	MgO	6,077	10,939	Anonymous
Nickel	NiO	1,006	1,811	Dulong
Oil, cotton seed		9,500	17,100	Anonymous
Oil, castor		8,848	15,926	Anonymous
Oil, coal, heavy		8,900	16,020	St. C. Deville
Oil, olive		9,862	17,751	Dulong
Oil, linseed		9,430	16,974	Anonymous
Oil, rape		9,489	17,080	Stohman
Oil, schist		9,000	1,620	Anonymous
Oil, sperm		10,000	18,000	Gibson
Paraffin	CO_2+H_2O liquid	11,140	20,050	Stohman
Paraffin	CO_2+H_2O liquid	10,340	18,612	Stohman
Peat		5,940	10,692	Bainbridge
Petroleum, crude		11,094	19,969	Mohler
Petroleum, refined		11,045	19,881	Mohler
Phosphorus	P_2O_5	4,509	8,116	Andrews
Phosphorus	P_2O_5	4,394	7,909	Abria
Pitch		8,400	15,120	Anonymous
Silicon	SiO_2	7,407	13,333	Berthelot
Stearic acid	CO_2+H_2O liquid	9,374	16,873	Stohman
Starch	CO_2+H_2O liquid	4,228	7,610	Berthelot
Sulfur, rhombic	SO_2	2,221	3,998	Favre & Silberman
Sulfur, rhombic	SO_2	2,166	3,899	Berthelot
Sulfur, monoclinic	SO_2	2,241	4,034	Thomsen
Tallow		9,500	17,100	Stohman
Tin	SnO_2	1,233	2,219	Dulong
Tin	SnO_2	1,144	2,059	Andrews
Turpentine		10,852	19,533	Favre & Silberman
Wood, beech, 12.9% H_2O		4,168	7,502	Gottlieb
Wood, birch, 11.8% H_2O		4,207	7,572	Gottlieb
Wood, oak, 13.3% H_2O		3,990	7,182	Gottlieb
Wood, pine, 12.2% H_2O		4,422	7,960	Gottlieb
Zinc	ZnO	1,301	2,342	Andrews
Zinc	ZnO	1,298	2,336	Dulong

THE CALCULATION OF THE HEAT OF COMBUSTION OF MIXED FUELS

The heating value of a mixed fuel is calculated from its constituents as found from ultimate analysis and any one of several formulas may be used for the determination. Dulong's formula is probably the most used and is given below along with Mahler's which has the same basic form. Practically every formula used is similar to the two given below.

$$\text{B.T.U. per lb. of Fuel} = 14650C + 62100(H - \tfrac{1}{8}O) \qquad \textit{Dulong}$$

$$\text{B.T.U. per lb. of Fuel} = 14650C + 62100H - 5400(O + N) \qquad \textit{Mahler}$$

where
C = Parts carbon in fuel
O = Parts oxygen in fuel
H = Parts hydrogen in fuel
N = Parts nitrogen in fuel

Example.—It is desired to find how many British Thermal Units will be developed by a pound of coal the ultimate analysis of which is:

Carbon = .7216
Oxygen = .0785
Hydrogen = .0496
Nitrogen = .0166

$$\text{B.T.U.} = (14650 \times .7216) + 62100\left(.0496 - \frac{.0785}{8}\right) = 13{,}043.02 \qquad \textit{Dulong}$$

$$\text{B.T.U.} = (14650 \times .7216) + (62100 \times .0496) - 5400(.0785 + .0166) = 13{,}138.06 \qquad \textit{Mahler}$$

The calorific value of the above coal as determined by tests of U. S. Geological Survey was 12,958 B.T.U.

HEATS OF FUSION OF CHEMICAL ELEMENTS AND INORGANIC COMPOUNDS

PHYSIKALISCH-CHEMISCHE TABELLEN, 1912

LANDOLT-BOERNSTEIN

Substance	Melting Point Deg. C.	Heat of Fusion in Kg. Calories		Authority and Date
		1-kilogram	1-gram-atom	
Bismuth	266.8	12.64	2.63	Person, 1849
Bismuth		12.4	2.58	Mazzotto, 1891
Bromine	−7.32	16.18	1.293	Regnault, 1849
Cadmium	320.7	13.7	1.54	Person, 1848
Chlorine	−103.5	22.96	0.184	Estreicher & Staniewski, 1910
Copper		43.0	2.74	J. W. Richards, 1903
Gallium	13	19.1	1.33	Berthelot, 1878
Iron, cast—white		32–34		Gruner, 1874
Iron, cast—gray		23		Gruner, 1874
Lead	325	5.86	1.21	Rudberg, 1830
Lead	326.2	5.37	1.11	Person, 1849
Lead		5.37	1.11	Mazzotto, 1891
Lead	322.4	5.32	1.11	Spring, 1886
Lead		6.45	1.34	Robertson, 1903
Mercury		2.84	0.57	Person, 1848
Mercury	−38.7	2.75	0.55	Pollitzer, 1911
Mercury	−38.7	2.85	0.57	Koref, 1911
Palladium	1500	36.3	3.86	Violle, 1878
Phosphorus	27.35	4.74	0.147	Pettersson, 1881
Phosphorus	29.73	4.74	0.147	Pettersson, 1881
Phosphorus	40.05	4.97	0.154	Pettersson, 1881
Phosphorus	44.2	5.034	0.156	Preson, 1848
Platinum	1779	27.2	5.3	Violle, 1877
Potassium	58	15.7	0.61	Joannis, 1887
Potassium		13.61	0.532	Bernini, 1906
Silver	999	21.1	2.28	Person, 1848
Sodium	96.5	31.7	0.73	Joannis, 1887
Sodium		17.75	0.408	Bernini, 1906
Sulfur	115	9.37	0.300	Person, 1848
Sulfur mono	119	10.4	0.33	Wiegand, 1908
Thallium	290	7.2	1.47	Robertson, 1903
Tin, ordinary, white	228	13.3	1.6	Rudberg, 1830
Tin, ordinary, white	232.7	14.25	1.70	Person, 1849
Tin, ordinary, white	227.3	14.65	1.74	Spring, 1886
Tin, ordinary, white		13.06	1.62	Mazzotto, 1891
Tin, ordinary, white		14.05	1.67	Robertson, 1903
Zinc	415.3	28.1*	1.84	Person, 1849
Zinc		28.0	1.8	Mazzotto, 1891

* Not reliable?

Inorganic Compounds

Substance	Melting Point Deg. C.	Heat of Fusion in Kg. Calories		Authority and Date
		1-kilogram	1-gram-mol.	
Aluminum bromide, $AlBr_3$		10.47	2.79	Kablukow, 1908
Ammonia, NH_3	−75	108.1	1.84	Massol, 1902
Antimony tribromide, $SbBr_3$	94.6	9.76	3.51	Tolloczko, 1901
Antimony trichloride, $SbCl_3$	73.2	13.29	3.01	Tolloczko, 1901
Arsenic tribromide, $AsBr_3$	31.0	8.93	2.81	Tolloczko, 1901
Barium chloride, $BaCl_2$	958.9	27.8	5.8	Plato, 1907
Caesium hydroxide, $CsOH$	272.3	10.7	1.61	v. Hevesy, 1910
Calcium chloride, $CaCl_2$	773.9	54.6	6.06	Plato, 1907
Calcium chloride, $CaCl_2.6H_2O$	28.5	40.7	8.9	Person, 1849
Calcium nitrate, $Ca(NO_3)_2.4H_2O$	42.4	33.49	7.94	Pickering, 1891
Carbon dioxide (5.10 atm.)	−56.29	43.8	1.93	Kuenen & Robson, 1902
Hydrogen peroxide, H_2O_2		2.70	9.18	de Forcrand, 1900

NOTES. For aluminum and iodine the only value available is the heat necessary to bring 1 kg. of the substance from 0° C. to the molten condition. It is, for aluminum, 239.4 kg. calories per kg. and for iodine 11.7 kg. calories per kg.

The value given by Smith is 334.21±0.08 joules. He assumes the mean calorie to equal 4.1832 joules.

Heats of Fusion—Chemical Elements, Inorganic Compounds

Substance	Heat of Fusion		Authority and Date
	1-kilogram	1-gram-mol.	
Ice	75.99	1.369	Pettersson, 1881
"	76.03	1.375	Pettersson, 1881
"	75.94	1.368	Pettersson, 1881
"	76.60	1.380	Pettersson, 1881
"	77.71	1.400	Pettersson, 1881
"	78.26	1.411	Zakrzewski, 1892
"	79.25	1.428	Person, 1848
"	79.06	1.424	Regnault, 1844
"	79.25	1.428	Regnault, 1844
"	80.025	1.442	Bunsen, 1870
"	79.24	1.428	Desains, 1843
" (See Note 2)	79.896± 0.02	1.440	A. W. Smith, 1903
"	79.61	1.435	Bogojawlenski, 1905
"	79.2	1.427	Leduc, 1906
"	79.67	1.436	W. A. Roth, 1908

Heats of Fusion—Chemical Elements, Inorganic Compounds (*Continued*)

Substance	Heat of Fusion 1-kilogram	Heat of Fusion 1-gram-mol.	Authority and Date
Iodine chloride, ICl	14.15	2.30	Berthelot, 1880
" " ICl α	16.42	2.66	Stortenbeker, 1892
" " ICl β	14.0	2.27	Stortenbeker, 1892
Lead bromide, $PbBr_2$	12.34	4.53	Ehrhardt, 1885
" "	9.9	3.65	Goodwin & Kalmus, 1909
Lead chloride, $PbCl_2$	20.90	5.81	Ehrhardt, 1885
" "	18.5	5.15	Goodwin &Kalmus, 1909
Lead iodide, PbI_2	11.50	5.30	Ehrhardt, 1885
Lithium nitrate, $LiNO_3$	88.5	6.10	Goodwin & Kalmus, 1909
Mercuric iodide, HgI_2	9.79	4.44	Guinchant, 1907
Nitric acid, HNO_3	9.54	0.601	Berthelot, 1877
Nitric oxide, N_2O_5	76.67	8.28	Berthelot, 1874
" " N_2O_4	32.2–37.2	2.96–3.42	Ramsay, 1890
Phosphoric acid, hypo. $H_4P_2O_6$	51.23	8.30	Joly, 1886
" " ortho. H_3PO_4	25.71	2.521	Thomsen, 1905
Phosphorous acid, hypo. H_3PO_2	35.00	2.31	Thomsen, 1905
" " ortho. H_3PO_3	37.44	3.072	Thomsen, 1905
Potassium chloride, KCl	86.0	6.41	Plato, 1906
dichromate, $K_2Cr_2O_7$	29.8	8.77	Goodwin & Kalmus, 1909
fluoride, KF	108.0	6.27	Plato, 1907
hydroxide, KOH	28.6	1.61	v. Hevesy, 1910
nitrate, KNO_3	47.37	4.79	Person, 1848
nitrate, KNO_3	25.5	2.57	Goodwin & Kalmus, 1909
Rubidium hydroxide, $RbOH$	15.8	1.62	v. Hevesy, 1910
Silver bromide, $AgBr$	12.6	2.37	Goodwin & Kalmus, 1909
chloride, $AgCl$	21.3	3.05	Goodwin & Kalmus, 1909
chloride, $AgCl$	30.7	4.40	Robertson, 1903
nitrate, $AgNO_3$	17.6	2.99	Guinchant, 1907
nitrate, $AgNO_3$	15.2	2.58	Goodwin & Kalmus, 1909
Sodium chlorate, $NaClO_3$	49.6	5.25	Goodwin & Kalmus, 1909
chlorate, $NaClO_3$	48.4	5.15	Foote & Levy, 1907
chloride, $NaCl$	123.5	7.22	Plato, 1906
chromate, Na_2CrO_4-$10H_2O$	36.0	12.3	Berthelot, 1878
chromate, Na_2CrO_4-$10H_2O$	39.2	13.4	Berthelot, 1878
fluoride, NaF	186.1	7.82	Plato, 1907
hydroxide, $NaOH$	40.0	1.60	v. Hevesy, 1910
nitrate, $NaNO_3$	62.97	5.355	Person, 1848
nitrate, $NaNO_3$	45.3	3.69	Goodwin & Kalmus, 1909
phosphate, Na_2HPO_4. $12H_2O$	66.8	23.9	Person, 1849
sulfate, Na_2SO_4. $10H_2O$	51.2	16.5	Cohen, 1894
thiosulfate, $Na_2S_2O_3$. $5H_2O$	37.6	9.3	v. Trentinaglia, 1876
Strontium chloride, $SrCl_2$	25.6	4.06	Plato, 1906
Sulfuric acid, H_2SO_4	8.77	0.860	Berthelot, 1874
H_2SO_4	24.031	2.358	Pickering, 1891
H_2SO_4	22.82	2.239	Knietsch, 1909
H_2SO_4	25.98	2.559	Bronsted, 1910
H_2SO_4. H_2O	31.72	3.68	Berthelot, 1874
H_2SO_4. H_2O	38.97	4.52	Luginin & Dupont, 1911
H_2SO_4. H_2O	39.92	4.63	Pickering, 1891
H_2SO_4. H_2O	34.91	4.05	Hammerl
H_2SO_4. H_2O	36.08	4.18	Hammerl
H_2SO_4. H_2O	38.38	4.45	Bronsted, 1910
Thallium bromide, $TlBr$	12.7	3.61	Goodwin & Kalmus, 1909
chloride, $TlCl$	16.6	3.98	Goodwin & Kalmus, 1909

BRIEF SUMMARY OF SOME IMPORTANT CHEMICAL LAWS AND HYPOTHESES

1. **Avogadro's Hypothesis.**—Equal volumes of all gases at the same pressure and temperature contain an equal number of molecules.

2. **Boyle's (or Mariotte's) Law.**—The volume of a gas at a constant temperature is inversely proportional to the pressure.

3. **Common Ion Effect—Repression of Ionization.**—Ionization is repressed by adding to the solution a salt which has a common ion with that of the solute.

4. **Complex Ions.**—These consist of a group of elements, possessing characteristics distinct from the elements of which they are composed. Example $K_4Fe(CN)_6$ ionized = K_4 and $Fe(CN)_6$. $KClO_3$ ionized = K and ClO_3.

5. **Conservation of Mass, Law of.**—The total weight of matter resulting from a combination or decomposition is always equal to the sum of the weights of the substances taking part in the reaction. In all chemical transformations except certain radioactive ones mass remains constant.

6. **Constant Proportion, Law of.**—The elements combine with one another in absolutely fixed relative proportions by weight.

7. **Dalton's Atomic Theory.**—All matter consists of an aggregate of minute particles, or atoms, which are chemically indivisible.

8. **Dalton-Henry's Law.**—The pressure exerted by a mixture of gases occupying a given volume is equal to the sum of the separate pressures which the different gases would exert if they alone occupied the given volume. Every gas behaves with respect to its own particular properties just as if it alone was present.

9. **Dulong-Petit's Law.**—All elements in the solid state have the same atomic heat. That is, elements taken in proportion to their atomic weights require equal quantities of heat in order to be raised to the same temperature.

10. **Electrolytic Dissociation Theory of Arrhenius.**—All substances which form solutions capable of conducting an electric current, the electrolytes, exist in solution, in part at least, as dissociated ions, atoms or atomic groups, carrying a definite charge of electricity. Each positive ion (cation) involves the presence of a negative ion (anion) carrying an equivalent amount of electricity.

When two oppositely charged poles are placed in such a solution, the positively charged anode attracts the negative particles in the solution and repels the positive, while the negatively charged cathode attracts the positively charged particles and repels those negatively charged, a flow of electricity thus being produced.

11. **Electromotive or Potential Series.**—Metals placed in solution tend to pass from a free element to the ionic condition, the more positive elements will displace the less positive from their ionic condition. See list of elements given in order of activity, in the table in the latter part of this volume.

12. **Faraday's Law.**—In equal periods of time a current of definite strength separates the ions from the solutions of electrolytes in quantities by weight, which stand in the same ratio to one another as their equivalent weights, i.e., their atomic weight divided by their valence.

The strength of an electric current can be measured by determining the weight of silver deposited at the cathode in a given time from a solution of silver, or by measuring the volume of hydrogen or oxygen produced from water by the action of the current.

13. **Gay-Lussac's Law (Charle's Law).**—At constant pressure, volumes of all gases increase on warming in the same proportion for every one degree.

The coefficient of expansion is 1/273 (0.003665). That is to say, for 1° C. increase in temperature the gas expands 1/273 of its volume. A volume of 273 ml. of gas at 0° C. would become 274 ml. at 1° C.

14. **Hess's Law of Constant Heat Summation.**—The evolution of heat which accompanies a chemical process is always the same whether the process takes place in one step or whether it passes through a number of intermediate processes.

15. **Lavoisier-Leplace's Law.**—Every compound has a certain heat of formation which is equal to its heat of decomposition.

16. **Mass Action, Law of (Guldberg-Waage's Law).**—The speed of reaction between two substances in solution is directly proportional, at any moment, to the molar concentrations of these reacting substances in solution, and to a constant, which is characteristic of the chemical nature of the reacting components, and of the temperature.

17. **Multiple Proportion, Law of.**—If two elements combine in more than one proportion, the masses of the one which combine with a given mass of the other bear a simple rational relation to one another, i.e., are always a whole multiple of the lowest.

Example: N_2O, N_2O_2, N_2O_3, N_2O_4, N_2O_5: the five oxides of nitrogen.

18. **Neuman-Kopp's Law.**—Molecular heat corresponds to the sum of atomic heats of the elements which constitute the molecule.

19. **Osmotic Pressure.**—A substance in solution produces the osmotic pressure, at a given temperature, which it would exert, if it were contained as a gas, at the same temperature, in the volume occupied by the pure solvent of the solution.

20. **Periodic Law of Mendeleeff.**—The properties of the elements are periodic functions of their atomic weights.

21. **Reversible Reaction.**—Compounds in solution resulting from a chemical reaction in turn react forming the original compounds present. This reversibility is prevented by removal from solution of one of the resulting compounds, by formation of an insoluble compound, which precipitates from solution, or a soluble complex or non-ionized substance, or by the formation of a gas which escapes. (See " Common Ion Effect.")

22. **Law of Electrostatic Force. Coulomb's Law.**—

$$F=\frac{q_1q_2}{Cd_2}.$$

F = force acting between two charged bodies.
q_1 and q_2 = quantities of electricity.
C = specific inductive capacity or dielectric constant of the medium.

23. **Law of Joule.**—

$h = rc^2t \times .2387 \times 10^{-7}$ calories
h = amount of heat evolved in a given time.
r = resistance to the passage of the current.
c = strength of the curretn.
t = time in seconds

24. **Ohm's Law.**—

$$C=\frac{E}{R}.$$

C = strength of current.
E = electromotive force.
R = resistance.

REAGENTS AND STANDARD SOLUTIONS[1]

This chapter consists of four sections, arranged as follows:

I. Common desk reagents: solutions, such as those of acids, bases, common organic solvents, special salts. A 10% solution means 10 ml. of a liquid or 10 g. of a solid diluted to 100 ml. (Approximate.)

II. Stock solutions of metallic or non-metallic ions for color matching, blank testing, etc. In this class belong solutions of arsenic, antimony, etc., for use in the Gutzeit tests, etc.

III. Primary standard substances, standard solutions and indicator solutions for precipitation and oxidation-reduction volumetric analysis. (Acids and alkalies and their indicators are treated in the chapter on this subject in Vol. II.)

IV. Organic reagents. Primarily the better known organic precipitants are given. A few color reagents are included.

I. COMMON DESK REAGENTS

Reagent Name	Per Cent	Vol. R.	Vol. H_2O	Res. sp.gr.	Approx. N	G. per ml.
Acetic acid, glacial	100	..	..	1.06	17	1.06
Acetic acid	80	..	..	1.07	15	0.84
Acetic acid, dilute	28	1	2	1.04	5	0.28
Hydrochloric acid, conc.	40	..	..	1.20	13	0.48
Hydrochloric acid, dil.	16	1	1.5	1.08	5	0.19
Nitric acid, conc.	96	..	..	1.50	23	1.43
Nitric acid, comm'l	70	..	..	1.42	16	1.00
Nitric acid, dil.	23	1	2	1.14	5	0.31
Sulfuric acid, conc.	95	..	..	1.84	36	1.77
Sulfuric acid, dil.	14	1	6	1.09	5	0.25
Ammonium hydroxide, conc.	28	..	..	0.90	15	0.26
Ammonium hydroxide, dil.	9	1	2	0.96	5	0.08
Sodium hydroxide	40	..	..	1.44	14	0.58
Sodium hydroxide, dil.	14	1	2	1.07	5	0.20

R = conc. reagent. Res. = resulting. N = normality. G. per ml. = grams of 100% reagent per ml.

Acetic Acid, Glacial.—C.P. 99.5% pure. Assay by titration and not by specific gravity because the 98% and the 80% solution have the same specific gravity, 1.067. The melting point determination gives results as good as those by titration. It is made after the manner of the "titer test" for acids, the tube being half filled, chilled to 10 to 11° C. and further chilled by placing the outside bottle in ice-water; the temperature of the super-cooled acid rises to its melting point, where it remains stationary for some time. The melting points of the acids of various strengths are as follows: 100%, 16.75°; 99.5%, 15.65°; 99%, 14.8° C.

Alcohol, Ethanol, 95%.—To free the alcohol from aldehyde before preparing alcoholic potash, treat 1 liter of the alcohol with 1.5 g. silver nitrate dissolved in 3 ml. of water and shake thoroughly; dissolve 3 g. of KOH in 15 ml. of warm

[1] Revised and expanded by the Editor (N. H. F.).

alcohol, cool add to the alcoholic silver nitrate and shake thoroughly, best in a tall bottle. Let the silver oxide settle, siphon off the clear liquid and distill, with freshly ignited and quenched (under water) pumice added to prevent bumping. Alcohol for the free acid determination is prepared by placing 10 10 to 15 g. of dry sodium carbonate in the reagent bottle, taking care to filter the solution before use.

Amyl Alcohol, C.P.

Alkaline Tartrate Solution.—See Tartrate Solution.

Ammonium Acetate.—70% solution. Use the salt, or cautiously add 1000 ml. of ammonium hydroxide to 1200 ml. of glacial acetic acid.

Ammonium Carbonate.—250 g. of powdered salt per liter of solution, containing 100 ml. of concentrated ammonium hydroxide. The solution contains approximately 22% of $(NH_4)_2CO_3$ $NH_4CO_2NH_2$.

Ammonium Chloride.—10% solution. 100 g. NH_4Cl per liter.

Ammonium Molybdate.—100 g. of pure molybdic acid are thoroughly mixed with 400 ml. of cold distilled water and 80 ml. of concentrated ammonia (sp.gr. 0.90) are added. When solution is complete, pour the ammonium molybdate slowly and with constant stirring into a mixture of 400 ml. of concentrated nitric acid (sp.gr. 1.42) and 500 ml. of distilled water. This order of procedure should be followed, since a difficultly soluble oxide of molybdenum is formed if the nitric acid is poured into the ammonium molybdate, and filtration will be necessary. Fifty mg. (0.05 g.) of microcosmic salt dissolved in a little water, are added to clarify the reagent; the precipitate is agitated, then allowed to settle for 24 hours and the clear solution is decanted through a filter into a large reagent bottle. Sixty ml. of the reagent should be used for every 0.1 g. of P_2O_5 present in the solution to be analyzed.

Ammonium Nitrate.—20% solution. 200 g. of NH_4NO_3 per liter.

Ammonium Oxalate.—4% solution. 40 g. of $(NH_2)_2C_2O_4 \cdot 2H_2O$ per liter.

Ammonium Phosphate.—10% solution. 100 g. of $(NH_4)_2HPO_4$ per liter. Sodium ammonium hydrogen phosphate, microcosmic salt, may be used instead, but diammonium phosphate is preferable.

Ammonium Sulfate.—25% solution. 250 g. of $(NH_4)_2SO_4$ per liter.

Ammonium Sulfide (Colorless).—Saturate 750 ml. of concentrated ammonia with hydrogen sulfide gas and add 500 ml. of concentrated ammonia and 1000 ml. of water

Ammonium Polysulfide (Yellow).—To a solution of ammonium sulfide made according to the preceding direction, add 75 g. of flowers of sulfur and shake thoroughly.

Barium Chloride.—A 10% solution. 100 g. of $BaCl_2 \cdot 2H_2O$ per liter.

Barium Chloride.—For sulfate determinations; 5% solution of the anhydrous salt or a 6% solution of the crystals.

Barium Hydroxide.—5% solution. 50 g. of $Ba(OH)_2 \cdot 8H_2O$ per liter.

Bromine.—Pure liquid bromine. An approximate N/3 solution is made by dissolving 26.6 g. of bromine in 1 liter of carbon tetrachloride.

Bromine-Potassium Bromide Solution.—320 g. of potassium bromide are dissolved in water barely sufficient to cause solution and mixed with 200 ml. of bromine, the latter being poured into the saturated bromide solution. After mixing well the solution is diluted to 2000 ml. Used for sulfur determinations.

Calcium Chloride.—10% solution. 100 g. of $CaCl_2 \cdot 6H_2O$ per liter.

Acid Calcium Chloride Solution.—Saturate a mixture of 90 parts of water and 10 parts concentrated HCl (sp.gr. 1.20) with calcium chloride.

Calcium Hydroxide (Lime water).—A saturated solution of $Ca(OH)_2$. Keep tightly stoppered; decant or filter before use.

Cinchonine Solution.—Dissolve 125 g. of the alkaloid in dilute HCl (1 part of acid to 1 of water) and diluting to 1 liter with HCl of the same strength.

Cinchonine Wash Solution.—30 ml. of the cinchonine solution and 30 ml. of concentrated HCl diluted to 1 liter.

Cinchonine Potassium Iodide Solution.—10 g. of cinchonine are dissolved by treating with the least amount of nitric acid that is necessary to form a viscous mass and taking up with about 100 ml. of water. The acid is added a drop at a time and an excess must be avoided. Twenty grams of potassium iodide are dissolved separately and the cinchonine solution is added. The resulting mixture is diluted with water to 1000 ml. After allowing the reagent to stand 48 hrs., any precipitate that forms is filtered off and the clear product is ready for use. The reagent preserved in a glass-stoppered bottle keeps indefinitely. It should be filtered free of suspended matter before use.

Citric Acid.—One part of acid in 3 parts of water. One hundred ml. of nitric acid should be added to each liter to prevent growth of moulds.

Citrate of Ammonia.—25 g. of the salt per 50 ml. of water.

Cuprous Chloride, Acid, for Gas Analysis.—The following simple method is effective: Cover the bottom of a two-liter bottle with a layer of copper oxide or "scale" 3/8" deep; place in the bottle a number of pieces of rather stout copper wire reaching *from the top to the bottom*, and sufficient to make a bundle an inch in diameter; fill the bottle with HCl of sp.gr. 1.10 (approx.). The bottle is shaken occasionally, and when the solution is colorless, or nearly so, it is poured into half-liter reagent bottles, containing copper wire, ready for use. The space left in the stock bottle should be filled immediately with hydrochloric acid (sp.gr. 1.10).

By adding copper wire, oxide or acid when necessary, a constant supply of this reagent may be kept on hand.

The *absorption capacity* of the reagent per ml. is 15 ml. of CO according to Winkler; and 4 ml. according to Hempel.

Care should be taken that the copper wire does not become entirely dissolved and that it extend from the top to the bottom of the bottle; further, the stopper should be greased thoroughly in order to exclude air more completely and thus avoid oxidation of the cuprous salt (indicated by brown color) and weakening of the absorbing power.

Cuprous Chloride, Ammoniacal, for Gas Analysis.—The acid cuprous chloride is treated with ammonia until a faint odor of the latter is perceptible; copper wire should be kept in the solution just as with the acid reagent. The alkaline solution has the advantage that it can be used when traces of hydrogen chloride might be harmful to subsequent determinations, as, for example, in the determination of hydrogen by absorption with palladium. It has the further advantage of not soiling mercury as does the acid reagent.

Absorption Capacity.—1 ml. absorbs 1 ml. of CO.

Cuprous chloride is at best a poor reagent for the absorption of carbon monoxide; to obtain the greatest accuracy where the reagent has been much

used, the gas should be passed into a fresh pipette for final absorption, and the operation continued until two successive readings agree. The compound formed by the absorption-possibly Cu_2COCl_2—is very unstable, as carbon monoxide may be freed from the solution by boiling or placing it *in vacuo*. Even if the reagent is shaken with air the gas is given off as is shown by increase in volume and subsequent diminution when the gas is shaken with fresh reagent.

Devarda's Alloy.—Forty-five parts of aluminum, 50 parts of copper and 5 parts of zinc. The aluminum is placed in a Hessian crucible in a furnace until the aluminum begins to melt, copper is now added in small portions until liquified and zinc is then plunged into the molten mixture. The liquid is heated for a few moments, covered and then stirred with an iron rod, allowed to cool slowly with the cover on and the crystallized mass is pulverized.

Ferric Chloride.—10% solution. 100 g. of $FeCl_3 \cdot 6H_2O$ per liter.

Ferric Nitrate.—One part of the salt in 6 parts of water. It is well to add a little nitric acid to prevent hydrolysis.

Hydrochloric Acid, Arsenic-free.—The commercial acid is treated with potassium chlorate to oxidize the arsenic to its higher form and the acid distilled. The distilling apparatus may be arranged so that constant distillation takes place, acid from a large container dropping slowly into a retort containing potassium chorate; fresh hydrochloric acid is supplied as fast as the acid distills. See Fig. 13, page 104.

Hydrogen Peroxide.—30% solution. If this is not available sodium peroxide added to sulfuric acid will serve for many of its applications.

Lead Acetate Test Paper (H_2S Removal).—Large sheets of qualitative filter paper are soaked in a dilute solution of lead acetate and dried. The paper is cut into strips 7×5 cm.

Lead Acetate Cotton Preparation.—A roll of absorbent cotton is opened and saturated with a 10% solution of lead acetate, and the surplus drained off. The material is dried on a line in a warm place away from hydrogen sulfide, rather than in an oven. The dry material is stored in a stoppered bottle until needed.

Magnesium Ammonium Chloride. Magnesia Mixture.—For precipitation of ammonium magnesium phosphate, 110 g. of magnesium chloride ($MgCl_2 \cdot 6H_2O$) are dissolved in a small amount of water. To this are added 280 g. of ammonium chloride and 700 ml. of ammonia (sp.gr. 0.90); the solution is now diluted to 2000 ml. with distilled water. The solution is allowed to stand for several hours and then filtered into a large bottle with glass stopper. Ten ml. of this solution should be used for every 0.1 g. of P_2O_5 present in the sample analyzed. For quantitative use the reagent should be prepared frequently in small lots, or if prepared in large lots should be stored in a resistant vessel. For qualitative use the solution must be filtered if any sediment of silica appears.

Magnesia Wash Solution.—Dissolve 100 g. of NH_4NO_3 in water, add 335 ml. of concentrated NH_4OH and dilute to 1000 ml.

Manganous Sulfate Solution.—Dissolve 48 g. of manganous sulfate in 100 ml. of water.

Mercuric Chloride.—Saturated solution of $HgCl_2$ (60–80 g. per liter). The solubility rises rapidly with temperature rise).

Mercuric Chloride.—5% solution. 50 g. of $HgCl_2$ per liter.

Mercuric Chloride or Bromide Paper, Sensitized.—20×20 in. Swedish Filter Paper No. 0 is cut into four equal squares. For use in the large Gutzeit apparatus the paper is dipped into a 3.25% solution of mercuric chloride (mercuric bromide may be used in place of the chloride) or if it is to be used in the small Gutzeit apparatus, it is dipped into a 0.35% mercuric solution. (The weaker the solution the longer and less intense will be the stain.) The paper should be of uniform thickness, otherwise there will be an irregularity in length of stain for the same amount of arsenic. See Chapter on Arsenic.

Nessler's Solution.—Dissolve 50 g. of potassium iodide in the smallest possible quantity of cold water. Add a saturated solution of mercuric chloride until a faint show of excess is indicated. Add 400 ml. of 50% KOH solution. After the solution has clarified by settling, make up to 1 liter with water, allow to settle and decant; solution used for determining NH_3 in water.

Palladous Chloride.—Five grams of palladium wire are dissolved in a mixture of 30 ml. of HCl and 2 ml. of HNO_3; the solution is evaporated just to dryness on a water bath, treated with 5 ml. of HCl and 25 ml. of water, and warmed until solution is complete. Upon dilution to 750 ml. the solution contains about 1% of palladous chloride and will absorb about two-thirds of its volume of hydrogen.

Paraffin.—Dissolve in carbon tetrachloride and use solution for covering reagent labels.

Peroxide Solution.—Dissolve 4 g. of sodium peroxide in 125 ml. of dilute sulfuric acid (1 vol. acid to 3 of water) and dilute to 500 ml. Used in titanium colorimetric determinations.

Potassium Ferricyanide.—The salt should be free of ferrocyanide, since the latter produces a blue color with ferrous salts. A crystal the size of a pinhead is dissolved in 50 ml. of water. The solution is made up fresh for each set of spot tests.

Potassium Fluoride Solution.—Dissolve 100 g. of potassium fluoride in about 1200 ml. of hot CO_2-free water; neutralize with hydrofluoric acid or potassium hydroxide as the reagent may require, using 5 ml. of phenolphthalein as indicator. Dilute sulfuric acid may be used in place of hydrofluoric acid in the final acid adjustment to get a neutral product. One ml. of the solution in 10 ml. of CO_2-free water should appear a faint pink. The concentrated mixture is filtered if necessary and then diluted to 2000 ml. with CO_2-free water. The sp.gr., will now be approximately 1.32 or about 35° Baumé. One ml. contains 0.5 g. of potassium fluoride.

Potassium Hydroxide.—(*a*) For carbon dioxide determinations, 500 g. of the commercial hydroxide are dissolved in 1 liter of water. *Absorption capacity:* 1 ml. absorbs 40 ml. of CO_2.

(*b*) For the preparation of potassium pyrogallate for special work, 120 g. of the commercial hydroxide are dissolved in 120 ml. of water.

Potassium Iodide Solution.—Dissolve 250 g. of potassium iodide, free from iodate, in distilled water and dilute to 1000 ml.

Potassium Permanganate.—For oxidation purposes. A 2% solution filtered free of the dioxide is required.

Potassium Pyrogallate.—Except for use with the Orsat or Hempel apparatus, this solution should be prepared only when wanted. The most convenient method is to weigh out 5 g. of the solid acid on paper, pour it into a

funnel inserted in the reagent bottle, and pour upon it 100 ml. of potassium hydroxide containing 120 g. of KOH. The acid dissolves at once, and the solution is ready for use. Attention is called to the fact that the use of potassium hydroxide purified by alcohol has given erroneous results. *Absorption capacity.* 1 ml. absorbs 2 ml. of oxygen.

Schiff's Fuchsin Bisulfite Reagent.—See Index.

Sodium Bismuthate.—Prepare as follows: Heat 20 parts of sodium hydroxide to redness in an iron or nickel crucible, and add in small quantities at a time, 10 parts of basic bismuth nitrate, previously dried in an oven. Then add 2 parts of sodium peroxide and pour the brownish yellow fused mass on an iron plate to cool; when cold, break it up in a mortar, extract with water, and collect on an asbestos filter. The residue after being washed four or five times by decantation is dried in a water oven, then broken up and sieved to give a finely powdered product.

Sodium Carbonate.—10% solution. 100 g. of Na_2CO_3 per liter.

Sodium Hydroxide.—Standard solutions—See Acidimetry and Alkalimetry, Vol. II. Also Alkalimetric Determination of Phosphorus.

Sodium Hydroxide Solution, Alcoholic.—Dissolve pure sodium hydroxide in 95% alcohol in proportion 22 g. NaOH per liter. Let stand in a stoppered bottle. Decant the clear liquid into another bottle and keep well stoppered. This solution should be colorless or only slightly yellow when used; it will remain colorless longer if the alcohol is previously treated with NaOH (about 80 g. to 1000 ml., kept at about 50° C. for 15 days and then distilled.

Sodium Sulfide.—10% solution, made from colorless crystals. Sodium sulfide may be made by saturating a concentrated solution of sodium hydroxide with hydrogen sulfide, then adding an equal volume of the sodium hydroxide. The solution is diluted to the required volume, allowed to stand several days, and filtered.

Sodium Metabisulfite.—Solid salt, $Na_2S_2O_5$.

Sulfuric Acid.—See Acidimetry and Alkalimetry Vol. II.

Stannous Chloride Solution.—60 g. of the crystallized salt are dissolved in 600 ml. of concentrated HCl and made up to one liter. The solution should be kept well stoppered.

Starch Solution.—5 g. of potato or arrowroot starch are rubbed up to a paste with cold water, and the paste is poured into 2 liters of boiling distilled water. (Soluble starch preparations are convenient to use.)

Preservatives.—Various substances may be used: (*a*) 2 mg. of mercuric iodide added to the hot solution; (*b*) A few ml. of 5% NaOH added to the hot solution; (*c*) 10 ml. of 1% solution of salicylic acid per liter of starch solution; (*d*) A few drops of chloroform per liter of the starch solution; (*e*) A few ml. of 10% $ZnCl_2$ solution per liter of starch. (*f*) Sodium chloride and acetic acid.—The starch solution is prepared by adding 500 ml. of a saturated solution of sodium chloride (filtered), 100 ml. of 80% acetic acid and 3 g. of starch, mixing the substances in the cold, then boiling about 2 minutes. A solution thus prepared keeps indefinitely.

Tartrate Solution, Alkaline.—25 g. of C.P. sodium potassium tartrate, $NaKC_4H_4O_6 \cdot 4H_2O$, is dissolved in 50 ml. of water. A little ammonia is added and then sodium sulfide solution. After settling for some time the

reagent is filtered. The filtrate is acidified with hydrochloric acid, boiled free of H_2S, again made ammoniacal and diluted to 100 ml.

Thymol Solution 1%.—The thymol is dissolved in a little glacial acetic acid containing 10% ethyl alcohol, and this solution is added to concentrated sulfuric acid. Addition of the thymol directly to the acid would produce a colored solution. The reagent should be kept protected from strong light, otherwise it will become colored.

Zinc, Amalgamated.—Mercuric chloride in sufficient quantity to make 1–2% of mercury in the amalgam is dissolved in a suitable volume of water, and the zinc (shot, or feathered 20 mesh) is poured into the mercury solution. In a few minutes the amalgam is washed well by decantation with distilled water. If the amalgam is to be used immediately it should be kept under distilled water; otherwise the powder should be dried and bottled. (Per 1 kg. of zinc use 13.5–27 g. mercuric chloride dissolved in 1 liter of water.)

II. STOCK SOLUTIONS OF METALLIC OR NON-METALLIC IONS

In this section are given directions for preparation of solutions for color matching tests, etc. The solutions should be prepared accurately from materials of known purity using good quantitative technique.

Ammonium Chloride.—Dissolve 3.82 g. of ammonium chloride in 1 liter of distilled water. Dilute 10 ml. of this solution to 1 liter with ammonia-free water. 1 ml. = 0.00001 g. of nitrogen. Used in water analysis.

Arsenic Standard Solution.—One gram of resublimed arsenious oxide, As_2O_3, is dissolved in 25 ml. of 20% sodium hydroxide solution (arsenic free) and neutralized with dilute sulfuric acid. Dilute with fresh distilled water to which 10 ml. of conc. H_2SO_4 have been added, to a volume of 1000 ml. Ten ml. of this solution is again diluted to 1 liter with the distilled water plus 1% sulfuric acid. One ml. of the final solution contains 0.001 mg. of As_2O_3. Used in arsenic determinations by Gutzeit and Marsh methods.

Standard Antimony Solution.—A stock solution is made up by weighing out 0.553 g. of $KSbOC_4H_4O_6$ which is dissolved in distilled water and diluted to 2000 ml. which represents 0.0001 g. Sb per ml.

From the above stock solution take 100 ml. and make up to 1000 ml.; this solution now contains 0.00001 g. Sb per ml., and it is used for making standard stains and for color comparison purposes.

Bismuth Standard Solution.—One gram of metallic bismuth is dissolved in the least amount of (1 : 1) nitric acid that is necessary to keep it in solution and diluted to 1000 ml. in a calibrated flask. One hundred ml. of this solution is diluted to 1000 ml. One ml. of this diluted solution contains 0.0001 g. of bismuth.

Copper Standard Solution.—One g. of purest electrolytic copper is dissolved in 20 ml. of dilute nitric acid, sp.gr. 1.2 and the solution is made up to 1000 ml.

Standard Iron Solutions.—(1) A ferric solution, the iron content of which has been determined, is diluted and divided so as to obtain 0.0004 g. of Fe. This is made up to 2 liters with water containing 200 ml. of iron-free C.P. H_2SO_4. One hundred ml. of this solution, together with 10 ml. of N ammo-

nium thiocyanate solution, is used as a standard. One hundred ml. contain 0.00002 g. of Fe.

Normal ammonium thiocyanate contains 76.1 g. NH_4CNS per liter.

(2) 8.6322 g. of ferric ammonium alum are dissolved in dilute hydrochloric acid and made up to 1 liter. The iron is determined in 100 ml. portions by the bichromate method. One ml. will contain about 0.001 g. of iron.

Standard Lead Solution.—A convenient solution is made by dissolving 0.1831 g. of lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, in 100 ml. of water and adding a few drops of acetic acid if necessary to clear up the cloudiness (basic salt) and diluting to 1000 ml. When 10 ml. of this solution are diluted to 1000 ml. each ml. of the resulting solution contains 0.000001 g. Pb.

Harcourt has suggested a permanent standard made by mixing ferric, copper and cobalt salts. For example, 12 g. of $FeCl_3$ together with 8 g. of $CuCl_2$ and 4 g. of $Co(NO_3)_2$ are dissolved in water, 400 ml. of hydrochloric acid added and the solution diluted to 4000 ml. 150 ml. of this solution together with 115 ml. of hydrochloric acid (1 : 2) diluted to 2000 ml. will give a shade comparable to that produced by the standard lead solution above, when treated with the sulfide reagent. The exact value per ml. may be obtained by comparison with a lead standard.

Potassium Nitrate Standard.—Recrystallize the purest obtainable material and dry first at 100° and then at 210° C. to constant weight. Chlorides, sulfates, carbonates, Ca, Mg, and Na are tested for and if present are determined and corrections applied.

Used as a standard in the Devarda method for determining nitrate.

III. PRIMARY STANDARDS; STANDARD SOLUTIONS: INDICATORS: PRECIPITATION AND OXIDATION-REDUCTION REACTIONS

In this section are found data on some of the most frequently used standard substances, standard solutions and indicators for *precipitation* and *oxidation-reduction reactions.* The standards, standard solutions and indicators for the field of Acidimetry and Alkalimetry are given in the chapter on this subject in Vol. II.

Volumetric reagents should be standardized at 20° C. if possible. The temperature at the time of standardizations should be noted in order to be able to correct for temperature variations during the use of the solution. A rise in temperature expands the solution and makes the concentration of the dissolved substance lower per ml., whereas a fall in temperature has the opposite effect.

Primary Standard Substances

If pure substances or substances of known purity are available the solution may be made up to any desired exact normality by weighing the standard substance and diluting it to the calculated volume. In many cases it is not advisable to use the foregoing " direct method," but to make up a solution of approximately known normality and then to standardize the solution by using it to titrate measured samples of a solution or better weighed samples of a primary standard substance. When the data are found it is desirable to note on the vessel the date of preparation, molar concentration, normality,

temperature of preparation, etc. Instead of expressing the concentration in terms of normality (5 N, N, 0.1 N, etc.) many prefer to use a factor which will convert the ml. of solution used into the equivalent of solution of some exact normality, as for example 0.5000 N, 0.1000 N, etc.

Illustration.—Suppose 52.50 ml. of a solution were equivalent to 55.00 ml. of normal solution; the factor is:

$\frac{55.00}{52.50} = 1.048$. Any volume of the solution used in a titration would if multiplied by the factor 1.048 give the number of ml. of exactly 1.000 N solution used.

In general the factor equals the ratio of the number of ml. used to the number of ml. of a theoretically correct solution.

The expression of the concentration of a solution on the normality basis makes the calculations simple and of similar pattern for all types of volumetric processes. To find the weight of some desired substance:

$$V \times N \times \text{m.e.} = \text{wt. of substance desired},$$

where V = ml. of standard solution used in a titration,
N = Normality of the standard solution used in the titration,
m.e. = The milliequivalent (1/1000th of the Eq. wt.) of the substance sought.

Primary Standards.—It is possible to set up a consistent set of solutions for all branches of volumetric analysis with the aid of very few pure substances. Two or three appropriate substances from the list: Arsenious oxide; potassium bi-iodate ($KH(IO_3)_2$); potassium acid phthalate; potassium bicarbonate; potassium dichromate; potassium bromate; potassium iodate; silver; sodium carbonate (from the bicarbonate); constant boiling hydrochloric acid; sodium oxalate. For work of good quality the standards should be pure to better than 99.9%. Arsenious oxide, sodium oxalate, potassium acid phthalate benzoic acid and certain other substances may be obtained from the National Bureau of Standards at moderate cost. It is fairly easy to purify many of the substances by 1 to 3 recrystallizations of materials of the quality sold for analytical reagent use.

A. Precipitation Reactions

Ammonium Molybdate.—4.75 g. of the salt are dissolved and made up to 1 liter. One ml. is equivalent to approximately 1% of Pb if a half gram sample is weighed for analysis. Used in lead determinations.

Ammonium Thiocyanate.—See Potassium Thiocyanate.

Eosin, Indicator Solution.—Dissolve 0.5 g. of the sodium derivative, $C_{20}H_4Br_4O_5Na_2$, in 100 ml. of water. Suitable indicator for the titration of bromide, iodide or thiocyanate with silver nitrate.

Ferric Indicator.—Saturated solution of ferric ammonium alum. If the alum is not available, $FeSO_4$ may be oxidized with nitric acid and evaporated with sulfuric acid to expel nitrous fumes. A 10% solution is desired. Five ml. of either reagent is used per titration. Used in titrating silver by the Volhard method.

Fluorescein, Indicator.—A 0.2% solution of sodium fluoresceinate (Uranin) in water, or 0.2% solution of fluorescein in alcohol is used. Used in the titration of chloride, bromide or iodide with silver.

Dichlor(R)fluorescein Indicator.—A 0.1% solution of the sodium salt in water or of the acid in 60–70% alcohol is used. This indicator is well adapted for the determination of chloride in water supplies; fluorescein is not satisfactory for use in water analysis.

Potassium Chloride.—Primary standard for silver solutions. The reagent salt may be further purified, if necessary, by precipitating the potassium chloride from a nearly saturated solution by leading hydrogen chloride gas into the solution through an inverted funnel. The precipitated potassium chloride is collected on a sintered glass or other suitable filter medium, washed sparingly with cold saturated KCl solution (from purified material), dried and heated to fusion in a platinum vessel. The material is powdered and bottled while still hot.

Potassium Ferrocyanide, Standard Solution for Zinc Determination.—21.12 g. of the crystallized salt (trihydrate) per liter. One ml. of the solution is equivalent to about 1% of Zn in a 0.5 g. sample.

Standardization. Low's Method.—Weigh carefully 0.2 g. of pure zinc, place in an 8-oz. flask and add 10 ml. of conc. HCl (sp.gr. 1.2). When the zinc has dissolved, dilute with 25 ml. of water, add a few drops of litmus solution and make slightly alkaline with ammonia. Again acidify with HCl adding 3 ml. in excess. Dilute to about 250 ml. with hot water and titrate with the ferrocyanide solution using a 15% uranium nitrate solution as an outside indicator, making the tests by the usual spot-plate technique. A brown tinge obtained by adding a drop of the solution titrated to a drop of uranium nitrate on a white tile is the end-point desired. It is advisable to divide the solution and to reserve a portion which is added near the end-point, in order to avoid overstepping the end-point. (See Chapter on Zinc for use of internal indicators.)

Potassium Ferrocyanide for Zinc Determinations.—42.24 g. of the pure crystallized reagent are dissolved and made up to 1 liter. One ml. = approximately 0.010 g. Zn. The solution should be allowed to stand about 4 weeks before using.

Standardization. New Jersey Zinc Co. Method.—Weigh into tall 400-ml. beakers several portions of pure zinc of about 0.35 g. each. Cover with water and add 10 ml. of HCl, sp.gr. 1.2, to dissolve. Now add 13 ml. of ammonia, sp.gr. 0.90, then make acid with HCl and add 3 ml. in excess. Add 0.03 or 0.04 mg. of ferrous iron in the form of ferrous sulfate solution and dilute to about 200 ml. with distilled water. Heat to boiling and titrate as follows: About ¼ of the solution is reserved in a small beaker and the ferrocyanide is added to the main solution with vigorous stirring. The solution takes on a blue color which changes to a creamy white when an excess of ferrocyanide is added. Now add a few ml. more and pour in the reserved portion of the zinc solution, excepting about 5–10 ml. Add ferrocyanide until the end-point is reached and add about ½ ml. more. The last of the reserved zinc solution is then poured into the beaker, washing out the small beaker with a portion of the main solution, and the ferrocyanide is added drop by drop until the

blue color fades sharply to a pea-green with one drop of ferrocyanide. This is the end-point. Repeat until concordant values are obtained for the normality.

Potassium or Ammonium Thiocyanate, 0.1 N Solution.—About 8 g. of ammonium or 10 g. of potassium thiocyanate are dissolved in water and diluted to 1 liter. The normality of the solution is determined by titrating aliquot portions of standard silver nitrate, or by titrating the solutions of separate weighed portions of pure silver.

Silver Nitrate Standard Solution, 0.1 N.—This solution contains 10.788 g. of Ag or 16.989 g. of $AgNO_3$ per liter. The silver nitrate dried at 120° C. or pure silver may be used; the required weight of the latter may be dissolved in nitric acid and made to 1 liter. If pure materials are not available a solution may be prepared of approximately 0.1 N concentration and standardized against pure NaCl.

Silver, Preparation of Pure Metal.—The volumetric methods used for the determination of silver in materials rich in silver require silver of high purity. The electrolytic method described below is preferred by many laboratories which are suitably equipped.

By Knorr's method, a solution of silver nitrate from which excess of nitric acid has been removed by evaporation is freed of metallic impurities by precipitating about 1/10th of the silver with sodium carbonate, boiling and filtering. The silver in the filtrate is precipitated by adding sodium carbonate, and the precipitate is decomposed without addition of reducing agent by melting in a crucible. Excess sodium carbonate carried down by the precipitate serves to cover the melt; the sodium carbonate that adheres to the metal is removed by hydrochloric acid. The metal is smelted under charcoal. Weighed portions are used for the standardization.

Sodium Chloride.—Analytical reagent grade material may be purified, if qualitative tests indicate this to be necessary, in the same manner as described for potassium chloride. The pure material is dried and 5.845 g. are made up to 1 liter for 0.1 N solution.

B. Oxidizing and Reducing Agents; Oxidation-Reduction Indicators

In this section there are listed alphabetically the most frequently used standard substances, standard solutions and indicators, together with certain standardization procedures and literature references to leading articles or review papers.

Arsenious Oxide, Primary Standard.—Obtainable from the National Bureau of Standards. The reagent grade article may be further purified, if qualitative tests prove this to be necessary, by dissolving the oxide in hot HCl, filtering the hot saturated solution, cooling, decanting, washing the oxide free of acid, drying and finally subliming. For methods of testing the purity of commercial arsenious oxide see I. M. Kolthoff, Vol. Analysis, II, p. 362 (translation by N. H. Furman, publ. by John Wiley & Sons, Inc., New York, 1929).

Standard Arsenite. Tenth Normal Arsenious Acid.—As_2O_3 is equivalent to 2 I_2, i.e. to 4 H; hence ¼ of the gram molecular weight of the oxide is the equivalent weight. $\frac{197.82}{4} = 49.455$ g. For 1 liter of 0.1 N solution 4.9455 g. is taken.

(*a*) *Solution for Titrating Iodine.*—Dissolve 4.946 g. of pure arsenious oxide in a warm solution of 10 g. of pure NaOH in 30–40 ml. of water. Dilute the solution to about 250 ml. and saturate it with carbon dioxide. Remove the tube, washing it thoroughly and letting the washings flow into the flask. Make the solution uniform after diluting to 1 liter. A solution prepared carefully in this manner is stable and does not need to be standardized.

Alternate Procedure.—The weighed quantity of arsenious oxide is dissolved by adding 2–3 g. of sodium hydroxide in a little water; the excess of alkali is neutralized with dilute sulfuric acid until a few drops of phenolphthalein indicator are just decolorized. Then 500 ml. of a solution of sodium bicarbonate (about 25 g.) are added; if the color returns add a few drops of sulfuric acid to destroy it. The solution is made up to the final volume.

If necessary, the reagent is standardized against an iodine solution or against weighed quantities of pure iodine.

(*b*) A convenient solution for standardizing various oxidizing agents (potassium permanganate, ceric sulfate, potassium bromate, potassium iodate, iodine) is made by dissolving 4.946 g. of the pure arsenious oxide in a solution of 2–3 g. of sodium hydroxide in 30–40 ml. of water. The solution is then made slightly acid with dilute sulfuric or hydrochloric acid and diluted to 1 liter.

Ceric Sulfate, Standard Solution.—The solution must contain enough sulfuric acid to prevent hydrolysis. For 0.1 N solutions prepared from the sulfate, the double sulfates, the oxide or from hexanitrato ammonium cerate the concentration of the acid should be 0.5–1 N. The following procedures give 1 liter of 0.1 N solution: (*a*) Dissolve 0.1 mole = 33.23 g. anhydrous ceric sulfate in 0.5–1 N sulfuric acid and make up to 1 liter with the acid. (*b*) Dissolve 63.25 g. of $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$ in 0.5–1 N sulfuric acid and dilute to 1 liter with the acid. (*c*) Dissolve 17.21 g. of pure CeO_2 or an equivalent amount of impure oxide in enough sulfuric acid to make the final acid concentration 1 N or slightly under. Pure ceric oxide must be heated with hot concentrated sulfuric acid in excess to convert it into the sulfate; the latter dissolves upon dilution of the solution. Crude oxide is transposed to the sulfate by heating at 120° C. with 1 : 1 sulfuric acid. (*d*) Dissolve 54.83 g. of $(NH_4)_2Ce(NO_3)_6$ in 0.5–1 N H_2SO_4 and make up to 1 liter with the acid. If applications are anticipated that nitrate would interfere with, the nitrate may be expelled by evaporating and heating to fumes of sulfur trioxide before diluting to the final volume.[2]

If the solution prepared in any of the foregoing ways deposits insoluble matter, the latter should be removed by filtration. Hexanitrato ammonium cerate gives promise of being obtainable 99.9% pure or better; the other substances are not readily obtainable in a state of purity at present.

Standardization Against Arsenious Oxide. Gleu's Procedure.[3]—To the solution of the arsenious oxide in sodium hydroxide is added enough sulfuric acid to make 20 ml. of 5 N after neutralizing the alkali. Add 0.15 ml. of 0.01 M osmium tetroxide (0.2555 g. OsO_4 in 100 ml. of 0.1 N sulfuric acid) and 3 drops of 0.01 M *o*-phenanthroline ferrous sulfate indicator, and dilute to 100 ml.

[2] G. F. Smith, V. R. Sullivan and G. Frank, Ind. Eng. Chem., Anal. Ed., 8, 449 (1936).
[3] K. Gleu, Z. anal. Chem., 95, 305 (1933).

Titrate with ceric sulfate to a sharp change from red to pale blue. Free HCl is not harmful up to 0.1 N concentration. The end-point is sharper in sulfuric acid solution.

If osmium tetroxide is not available use 5 ml. of 0.005 M iodine monochloride catalyst, and have 20 ml. of conc. HCl present per 100 ml. of the arsenic solution. Use chloroform or carbon tetrachloride as indicating layer (5 ml.) and titrate to the disappearance of the iodine color from the layer of solvent. Alternatively, the solution may be titrated using *o*-phenanthroline ferrous sulfate indicator and ICl catalyst, heating to 50° C. toward the end of the titration.[4] The color should not return within 1 minute at this temperature if the end-point has been reached.

Sodium oxalate may be used as a primary standard, and the conditions of titration are as described at the end of the last paragraph (ICl catalyst; temperature 50° C.).

Other good standard substances are pure electrolytic iron, the reduced solution of a sample of standard iron ore, the solution of pure dried potassium ferrocyanide, etc. In these latter instances diphenylamine, *o*-phenanthroline ferrous sulfate, erio green, etc., may be used as indicators.

The *applications* of standard ceric sulfate are very numerous and include the direct or indirect determination of the following: Sb, As, Pb, Ca, Cr, Fe, $Fe(CN)_6^{----}$, K, Cu, Mo, Na, NO_2^-, Hg^I, HN_3, H_2TeO_3, Tl, $S_2O_3^{--}$, Ti, U, V, Sn, I^-, and many organic acids, hydroquinones, and other substances.[5] One of the best applications of the reagent is in the titration of ferrous iron in the presence of HCl, $SnCl_4$ and Hg_2Cl_2 after reduction by stannous chloride. The indicators erio green, erio glaucine and *o*-phenanthroline ferrous sulfate are especially suitable for this titration.

Diphenylamine Indicator Solution.—Melt 1 g. of diphenylamine (m.p. 52.9° C.), add 100 ml. of conc. H_2SO_4 and shake the mixture for 15–30 seconds.[6] One to 3 drops (0.05 ml.) of this solution serve for the titration of ferrous solution with potassium dichromate (0.1 N) or the reverse. The solution titrated should contain 5 ml. of conc. H_2SO_4 or 10 ml. conc. HCl per 150–200 ml., and 15 ml. of a mixture of 150 ml. conc. H_2SO_4 and 150 ml. conc. H_3PO_4, sp.gr. 1.7 per liter. Knop[7] gave 0.05 ml. as the correction to be subtracted from the volume of the 0.1 N dichromate. This was not confirmed by Brennecke who found no correction.[8]

The correction depends upon the conditions of reaction; the amounts of correction for very dilute solutions have been determined and tabulated.[9] The uncertainty of the correction may be avoided by using oxidized indicator

[4] Willard and Young, J. Am. Chem. Soc., 55, 3260 (1933).

[5] For details see N. H. Furman, Chapter II, Neuere massanalytische Methoden, Vol. XXXIII, Margosches Series, F. Enke, Stuttgart, 1937. Translated by Oesper, D. Van Nostrand Co., New York. G. F. Smith, Ceric Sulfate. Publication of G. F. Smith Chemical Co., Columbus, O. Philena Young, J. Chem. Ed., 11, 466 (1934).

[6] Improved method of preparation due to H. M. State, Ind. Eng. Chem., Anal. Ed., 8, 259 (1936).

[7] J. Knop, J. Am. Chem. Soc., 46, 263 (1924).

[8] Op. cit. Neuere massanalytische Methoden.

[9] Tables of corrections are given in Neuere massanalytische Methoden, Chap. VI. E. Brennecke. This book is available in English translation by Oesper, D. Van Nostrand Co., New York.

solution.[10] A 0.1% solution of the indicator is prepared by dissolving 0.1 g. in 10 ml. of conc. H_2SO_4 and adding 90 ml. of glacial acetic acid. The equivalent of 100 ml. of 0.01 M indicator is oxidized with 25 ml. of 0.1 N $K_2Cr_2O_7$ after dilution to 300 ml. After the oxidizing agent has been slowly added, 8 ml. of 0.1 N ferrous sulfate are added. The resulting green solution is allowed to stand 3–4 days and the solution is siphoned away from the green precipitate which is the oxidized indicator. Centrifuging is effective for recovery of the product. The green precipitate is shaken with 100 ml. of water. Then 0.5 ml. of this suspension is equivalent in coloring power to 0.3 ml. of 0.01 M indicator. Such indicator solution gives a reliable blank or correction in titrations of chromium and vanadium with 0.025 N $FeSO_4$, 0.03 ml. of reagent per 0.1 ml. of indicator.

Diphenylamine Sulfonic Acid, Indicator Solution.—For use with 0.1 N solutions prepare the indicator stock solution by treating 0.32 g. of barium diphenylamine sulfonate in 100 ml. of water with 1 ml. of conc. H_2SO_4. The barium sulfate is removed by decanting the solution. In titrating ferrous solution there should be present 5 ml. of H_3PO_4, sp.gr. 1.70 and 5 ml. of conc. HCl or H_2SO_4 per 150–200 ml. and 0.3 ml. of the indicator.

Oxidized diphenylamine sulfonic acid may be prepared for use in titrations with very dilute solutions. See references under Diphenylamine. The diphenylamine sulfonic acid indicator has the advantages that tungsten and mercuric ion do not interfere with its use; the color change is brilliant and sharp.[11]

Diphenylbenzidine. The indicator solution is prepared like that of diphenylamine, and its uses are similar; the solution is not as stable as that of diphenylamine.

Erioglaucine A (or Alphazurine, Schultz No. 506) and Eriogreen B.

The use of these indicators in titrations with potassium permanganate was proposed by Knop,[12] and with ceric sulfate by Furman and Wallace.[12] Either substance is dissolved in water to give a 0.1% solution of indicator (0.1 g. per 100 ml.). If from 0.5 to 1 ml. of the indicator is used the correction amounts to about 0.02 ml. of 0.1 N ceric sulfate or potassium permanganate. The indicators are especially useful in the titration of ferrocyanide with either reagent, or in the titration of ferrous solutions with ceric sulfate. Other indicators of the triphenylmethane series are satisfactory.[13]

Fehling's Solution. For Determination of Sugar.—(*a*) Copper sulfate solution. Dissolve 34.639 g. of $CuSO_4 \cdot 5H_2O$ in water and dilute to 500 ml. (*b*) Alkaline tartrate solution. Dissolve 173 g. of Rochelle salts and 125 g. of KOH in water and dilute to 500 ml. (The Assoc. Off. Agr. Chem. Methods gives 50 g. KOH instead of 125 g.) Equal volumes of solutions (*a*) and (*b*) are mixed immediately before the solution is used.

Ferrous Sulfate, Standard. Reagent for Nitric Acid Determinations.

A. Reagent to Be Used in Titration of Nitric Acid in Sulfuric Acid, Oleum, etc.—176.5 g. of $FeSO_4 \cdot 7H_2O$ are dissolved in 400 ml. of water and 500 ml.

[10] Willard and Young, Ind. Eng. Chem., Anal. Ed., 5, 154 (1933).

[11] Kolthoff and Sarver, J. Am. Chem. Soc., 52, 4179 (1930); 53, 2902, 2906 (1931).

[12] J. Knop, Z. anal. Chem., 77, 111 (1929); Knop and Kubelkova, ibid., 77, 125 (1929); also 85, 401 (1931); Furman and Wallace, J. Am. Chem. Soc., 52, 2347 (1930).

[13] For a review see E. Brenneke, Neuere massanalytische Methoden, Chap. VI, transl. by Oesper, D. Van Nostrand Co., New York.

of 60% H_2SO_4 (1 vol. of 66° Bé acid per 1 vol. of H_2O) are added with constant stirring and the solution, cooled if necessary, is made up to 1000 ml. One ml. is equivalent to approximately 0.02 g. HNO_3, the exact value being determined by standardization.

B. Reagent for Titration of Nitric in Phosphoric or Arsenic Acid.—Ferrous sulfate is made by dissolving 264.7 g. $FeSO_4 \cdot 7H_2O$ in 500 ml. of water; 50 ml. of 66° Bé·H_2SO_4 (93.2%) are added and the solution is made up to 1000 ml. The exact concentration is determined by titrating a known amount of nitric acid in phosphoric or arsenic acid, warming to 40 or 50° C.

Ferrous Ammonium Sulfate.—The 0.1 N solution contains 39.213 g. of $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ per liter. Dissolve 39.5 g. of the salt in water and add enough sulfuric acid to prevent hydrolysis (as much as 10 ml. per liter may be present). Relatively permanent solutions may be prepared by storing them under hydrogen, nitrogen, or carbon dioxide. Standardize by titration with standard dichromate, permanganate or ceric sulfate solution.

Iodine Solution. Standard 0.1 N.—Dissolve 20–25 g. KI in the minimum volume of water and add 12.7 g. of iodine (resublimed; theoretical amount 12.692 g.) and dilute to 1000 ml. after all of the iodine has been dissolved in the small volume of KI solution. Preserve in a dark bottle or covered bottle, to shield the solution from the action of light.

Standardization.—Aliquot portions are titrated with standard thiosulfate or with standard arsenite. Alternatively, separate weighed portions of primary standard arsenious oxide may be dissolved and titrated.

For the determination of tin in tin plate an iodine solution is adjusted so that 1 ml. equals 0.0579 g. of tin. Then if a sample with a total surface of 8 sq. in. is taken, 1 ml. of the iodine solution is equivalent to 0.1 pound of tin per base box. Starch is used as the indicator.

Nitric Acid Standard-Ferrous Sulfate Method for Nitrates.—Standardization of the acid. 11.6 g. of standard potassium nitrate, equivalent to about 9.6 g. of $NaNO_3$ are dissolved and made to volume in a 100-ml. weighing bottle and 10 ml. are placed in the Devarda flask, reduced and the ammonia distilled and its value in terms of H_2SO_4, KNO_3 and $NaNO_3$ is stated on the bottle. Temperature must be noted, for the solution expands or contracts 0.029 ml. per degree centigrade above or below the temperature at the time of standardization.

***o*-Phenanthroline-Ferrous Sulfate Indicator.**[14]—A 0.025 molar ferrous sulfate solution is treated with enough *o*-phenanthroline monohydrate to make the solution 0.075 M in *o*-phenanthroline (Mol. wt. $C_{12}H_8N_2 \cdot H_2O = 198.2$). With 0.1 N solutions the indicator correction is negligible. The indicator is especially suited for titrations with ceric sulfate; it may also be used in permanganate titrations, or for titration of bichromate with ferrous sulfate; in the reverse titration the change is sluggish at the end-point.

Potassium Bromate.—This substance is readily obtained pure by recrystallization and drying at 150° C. For an 0.1 N solution the theoretical weight, 2.7835 g. (1/60th mol. wt.) is dissolved and made up to 1 liter. The solution is stable if prepared from a pure specimen; its best uses are in the determination

[14] Walden, Hammett and Chapman, J. Am. Chem. Soc., **53**, 3908 (1931); **55**, 2649 (1933); also **56**, 57 (1934). Willard and Young, ibid., **55**, 3260 (1933).

of arsenic, antimony and organic substances, the latter by bromination. See Chapters on Antimony and Arsenic.

Potassium Dichromate.—Many manufacturers supply reagent grade potassium dichromate of sufficient purity to be used as a primary standard.[15] The material is fused at the lowest possible temperature, then broken up and dried finally at 100–110° C. For a tenth normal solution 1/60th of the gram. molecular weight, or 4.903 g., is dissolved in water and made up to one liter. The solution is very stable if care is taken to exclude reducing substances.

If it is necessary to standardize the potassium dichromate solution the following methods may be recommended:

(1) *Against Pure Iron.*—About 0.25 g. of pure iron (electrolytic or prepared from iron carbonyl) is dissolved in an Erlenmeyer flask provided with a Bunsen valve. The air is displaced from the flask before adding the iron by treating 2 g. of sodium bicarbonate with 20 ml. of 5 N sulfuric acid. The metal is dropped in and a rubber stopper with the valve is inserted. When the reaction has ceased, the ferrous solution is titrated with potassium bichromate, after the addition of 0.3 ml. of 0.01 M diphenylamine sodium sulfate as indicator, and 10 ml. of phosphoric acid specific gravity 1.37 (1 volume of conc. phosphoric acid, sp.gr. 1.70+one volume of water). The titration must be slow near the end-point which is a change to purplish or blue-violet.

Other indicators may be used as, for example, one drop of 1% diphenylamine solution, etc. Alternatively, the external or spot-plate method may be used in which case no phosphoric acid is added to the iron solution, and the indicator is 1% potassium ferricyanide placed in drops on a white tile (spot-plate) provided with depressions. The end-point is, of course, found when a small drop taken from the solution fails to produce a blue color with a drop of the ferricyanide.

Since it is difficult to exclude air perfectly from the iron solution, one may reduce the iron after it has been dissolved by adding stannous chloride in slight excess to the hot solution, followed by 10 ml. of saturated mercuric chloride solution after the iron solution has been cooled and diluted to 150 ml. If the solution contains mercuric salt, sodium diphenylamine sulfonate indicator or the spot-plate method should be used.

(2) *Against Standard Iron Ore.*—A standard iron ore secured from the U. S. Bureau of Standards, Washington, D. C., may be used as a primary standard. The advantage of such procedure is that the standard contains the same substances in approximately the same percentages as many typical ores. For accurate work a chamber burette should be used; the graduations from 75–90 ml. are in tenths and from 90 to 100 ml. in twentieths of a ml. A titration of 90 to 100 ml. of N/5 solution would require 0.9 to 1.1 g. of iron or half of this amount for N/10 solution. If the ore contains 69% of iron a sample of $1\times\frac{100}{69}=1.45$ (approx.) g. would be suitable for N/5 solution. The solution, reduction and titration of the sample are performed as described in the chapter on Iron.

The iron value of the solution per ml. is:

$$1\text{ ml.}=\frac{\%\text{ Fe}\times\text{Wt. Sample}}{1}$$ divided by ml. dichromate used in the titration.

[15] Willard and Young, Ind. Eng. Chem., Anal. Ed. 7, 57 (1935).

Potassium Iodate.—The analytical reagent grade material may often be relied on to be 99.8 pure or better. The substance is readily purified by recrystallization from water and drying at 180° C. It is one of the most useful standard substances since thiosulfate may be standardized against it; also it will serve in the field of acidimetry. In the latter case weighed samples or aliquot portions of a standard solution of the iodate are treated with excess of KI solution and neutral sodium thiosulfate and methyl red indicator is added and the solution is titrated with the acid to be standardized. One ml. of N acid = 0.035669 g. KIO_3. Each ml. of N/10 (M/60) potassium iodate solution is equivalent to 1 ml. of 0.1 N acid. The standardization of thiosulfate is described under sodium thiosulfate.

A standard solution of potassium iodate may be used to determine a very great variety of inorganic or organic substances. It is especially useful for sulfur in steel, arsenic, antimony, copper (indirect through cuprous thiocyanate), hydrazine, etc. The titrations are made under "iodine monochloride conditions" in 4–6 M HCl solution. Ten ml. of 0.005 M ICl is used as a catalyst, and a layer of $CHCl_3$ (10 ml. as indicator). Disappearance of the iodine color from the chloroform layer marks the end-point; the titrations are made in a glass stoppered bottle.[16]

The iodine monochloride is prepared by dissolving 0.279 g. KI and 0.178 g. KIO_3 in 250 ml. of water and adding 250 ml. of conc. HCl. The solution is adjusted by adding dilute KI or KIO_3 to equivalence as indicated by chloroform or potentiometrically. The solution is 0.005 M in ICl.

Potassium Permanganate.—Convenient strengths to use for standard solutions are N/5, N/10, or N/20.

Since commercial potassium permanganate is seldom or never pure and since the substance reacts with organic matter or other reducing agents that may be present in distilled water, it is necessary to prepare the solution empirically and to standardize it.

Preparation.—One mole of potassium permanganate is equivalent to 5H. Therefore 1/5th of the molecular weight or 31.60 g. is needed for 1 liter of normal solution, or 3.160 g. would be needed for one liter of N/10 solution. It is advisable to use more than the theoretical amount, namely 3.25 g.

This quantity of the salt is dissolved in one liter of hot water. After standing twelve hours or longer, the solution is either siphonized through glass,[17] or filtered through asbestos in order to free it from manganese dioxide which catalyzes the decomposition of the reagent. The solution should be shielded from the action of light by using a dark bottle or a suitable covering for the bottle.

(*a*) *Standardization Against Sodium Oxalate.*—This process has been investigated at the National Bureau of Standards,[18] and it is recommended that the McBride procedure[19] be replaced by the following recommended procedure.

[16] G. S. Jamieson, Volumetric Iodate Methods, Chem. Catalog Co., 1926.

[17] If the siphoning process is used, the solution is allowed to stand in a tall cylinder until the MnO_2 has settled. The solution is siphoned off without disturbing the sediment.

[18] Fowler and Bright, J. Research Natl. Bur. Standards, 15, 493 (1935).

[19] McBride, J. Am. Chem. Soc., **34**, 393 (1912).

Procedure.—Transfer 0.3 g. of sodium oxalate (dried at 105° C.) to a 600-ml. beaker. Add 250 ml. of diluted sulfuric acid (5:95) previously boiled for 10 to 15 minutes and then cooled to 27±3° C. Stir until the oxalate has dissolved. Add 39 to 40 ml. of 0.1 N potassium permanganate at a rate of 25 to 35 ml. per minute while stirring slowly. Let stand until the pink color disappears (about 45 seconds). Heat to 55 to 60° C. and complete the titration by adding permanganate until a faint pink color persists for 30 seconds. Add the last 0.5 to 1 ml. dropwise with particular care to allow each drop to become decolorized before the next is introduced.

Determine the excess of permanganate required to impart a pink color to the solution. This can be done by matching the color by adding permanganate to the same volume of the boiled and cooled diluted sulfuric acid at 55° to 60° C. This correction usually amounts to 0.03 to 0.05 ml.

In potentiometric titrations the correction is negligible if the end-point is approached slowly.

$$\text{Equation: } 2KMnO_4 + 5Na_2C_2O_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2 \cdot \frac{Na_2C_2O_4}{2} = \frac{H_2C_2O_4}{2} = H$$

The equivalent weight of sodium oxalate is, therefore, one-half of its molecular weight or $\frac{134}{2} = 67$. The weight of sodium oxalate used divided by ml. of permanganate required, equals weight of sodium oxalate equivalent to 1 ml. of the permanganate, and this quantity divided by 0.067 gives the normality of the solution. Illustration: 0.2060 g. of sodium oxalate require 30.69 ml. permanganate. $\frac{0.2060}{30.69} = 0.006712$; then $\frac{0.006712}{0.067} = 0.1002$ normal.

(*b*) *Standardization Against Iron or Iron Compounds.*—If pure iron or pure ferric oxide or a standard iron ore of suitable composition is available, a solution containing a suitable quantity of iron (about 0.2 g.) is prepared, iron is reduced to the ferrous state and titrated with potassium permanganate. (See Procedure for Standardization of Potassium Bichromate against Iron.) If the solution contains hydrochloric acid, a suitable quantity of Zimmermann-Reinhardt mixture must be added before the titration. (See Chapter on Iron.)

(*c*) *Standardization Against Arsenious Oxide.*—Portions of a standard arsenite solution measured from the burette or a pipette (see section on standard arsenite solution) may be titrated with permanganate, or weighed samples of .2 g. each of arsenious oxide may be dissolved in alkali and acidified.

(1) *Lang's Procedure.*[20]—Add enough acid to make the solution 0.5–2N in hydrochloric acid or at least 0.5 N in sulfuric acid. Add 1 g. of sodium chloride and 1 drop of about 1/400 N iodide or iodate solution and titrate with potassium permanganate. If the solution contains no chloride it should be warmed to 40–50° and titrated after adding one drop of the catalyst.

(2) *Gleu's Procedure.*[21]—The Solution prepared as described under (1) should be acidified with 20–30 ml. of 5 N sulfuric acid and two drops of 0.01 M

[20] R. Lang, Z. anorg. allgem. Chem., **152**, 197 (1926).
[21] Gleu, Z. anal. Chem., **95**, 305 (1933).

osmium tetroxide solution added as a catalyst. The titration with potassium permanganate is then made.

Sodium Thiosulfate. Used in Copper Determinations.—7.5 g. of the salt, $Na_2S_2O_3 \cdot 5H_2O$, are dissolved and made up to 2 liters with water. The solution is standardized against a copper solution containing 1 g. of pure copper per liter, or 0.001 g. Cu per ml. The amount of copper used in the titration should be approximately equal to that in the ore, and all other conditions should be the same. For high grade ores and crude copper the standard solution should be ten times as strong as that above described. The copper solution is made slightly ammoniacal then acidified with acetic acid. Pure sodium or potassium iodate is added and the iodine liberated is titrated with the thiosulfate solution. See Chapter on Copper.

Sodium Thiosulfate, Standard 0.1 N Solution for General Analysis.—Sodium thiosulfate reacts with iodine as follows:

$$I_2 + Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$$

One gram molecule of the thiosulfate is equivalent to 1 gram atom of iodine. For 1 liter of 0.1 N sodium thiosulfate 0.1 mole, or $\frac{248.15}{10} = 24.815$ g. of $Na_2S_2O_3 \cdot 5H_2O$ is required; generally an excess—25 g. of the reagent salt—is used; if 5 or 10 liters is prepared, 125 or 250 g. would be weighed out. The material is dissolved in hot distilled water that has just been boiled to remove CO_2. For each liter, 0.1 g. of Na_2CO_3 should be added to the water. When prepared in this way the solution requires little or no aging (to allow CO_2 to be used up and sulfur to settle); otherwise the solution has to stand a week or 10 days.

Standardization.—Iodine sublimed from a mixture of lime and KI and then resublimed may be used for standardization. Pure potassium iodate or pure potassium dichromate may be weighed and allowed to liberate an equivalent amount of iodine from KI. If the resublimed iodine is used, the procedure is as follows: Dissolve 2–3 g. of pure KI in ½ ml. of water in a weighing bottle, stopper, let come to room temperature and weigh. Add 0.5 g. of the iodine, allow temperature to come to that of the room and reweigh, the increase due to iodine dissolved being noted. Open the bottle under 200 ml. of water containing 1 g. of KI and titrate. Divide wt. of iodine by ml. of thiosulfate to get wt. of iodine per ml. and divide the latter by the milliequivalent of iodine, 0.12692 to find the normality of the thiosulfate solution.

Dichromate and Other Standard Substances.—For 0.1 N solutions weigh 4.9035 g. $K_2Cr_2O_7$ or 3.5669 g. KIO_3 per liter, or proportionately smaller quantities for ½ or ¼ liter. Measure an appropriate volume of either 0.1 N solution into water containing 2–3 g. KI and 10 ml. dilute HCl per 200 ml. The acid solution should be freed of dissolved air (previous boiling, or treatment with CO_2). The iodine liberated is titrated with the thiosulfate solution. A glass-stoppered Erlenmeyer flask is convenient for storing the mixture for the period of 5–10 minutes that is necessary to complete the liberation of iodine. Pure potassium bromate may be used instead of the dichromate or the iodate. A previously standardized permanganate solution may be used to standardize the thiosulfate, but the process is less direct than the ones involving the weighing of pure standard substances. Ceric sulfate may only

be used in the reverse titration: A measured volume of the thiosulfate is diluted to 10 times its volume, 2 to 3 g. of KI and some starch indicator are added, and the mixture is titrated with the standard ceric solution.

Starch Solution.—See Section 1 of this Chapter.

Stannous Chloride Solution.—The reagent is prepared by dissolving 2 g. of stannous chloride crystals in hot conc. HCl and making up to 1 liter. The solution should be kept in a dark bottle provided with burette and attachments for excluding air. (See Fig. 58, p. 485.) The solution is protected from the oxygen of the air by passing the latter through alkaline pyrogallol when solution is transferred to the burette. It is advisable to restandardize every ten or fifteen days. One ml. of the solution is equivalent to about 0.001 g. of iron.

IV ORGANIC REAGENTS

In this section are given data on the better known organic precipitants for inorganic ions, together with a few color test reagents.[22]

In the following partial list of the elements there is given for each element a selection of reagents or color tests. The reagents are then considered in alphabetical order.

Selected List of Reagents for the Detection or the Determination of Certain Elements

Element	Reagents	Element	Reagents
Aluminum	Aluminon Oxine	Magnesium	*p*-Nitrobenzeneazo-resorcinol Oxine
Antimony	Phenylthiohydantoic acid	Mercury	Diphenylcarbazide Dithizone
Beryllium	Oxine Quinalizarin	Molybdenum	α-Benzoinoxime
Bismuth	Cupferron Dimercaptothiodiazol Dithizone Cupferron	Nickel	α-Benzildioxime Dimethylglyoxime Rubeanic acid Salicylaldoxime
Cadmium	Diphenylcarbazide Phenyltrimethyl-ammonium iodide Oxine	Nitrate	Diphenylamine sulfonic acid Nitron
Calcium	Picrolonic acid	Palladium	*p*-Dimethylamino benzylidenerhodanin Dimethylglyoxime α-Nitroso β-Naphthol
Chromium	s-Diphenylcarbazide		
Cobalt	Nitroso beta naphthol Rubeanic acid	Potassium	Dipicrylamine
Copper	α-Benzoinoxime Cupferron *p*-Dimethylamino-benzylidene rhodanin Dithizone Rubeanic acid Salicylaldoxime	Rhenium	Nitron
		Silver	*p*-Dimethylamino benzylidenerhodanin
		Sulfur (Sulfate)	Benzidine
		Thorium	Cupferron
		Tin	Cupferron
		Titanium	Cupferron
Fluoride	Triphenyltinchloride	Tungsten	Cinchonine
Iron	Cupferron	Vanadium	Cupferron
Lead	Dithizone Dimercaptothiodiazol Picrolonic acid Salicylaldoxime	Zinc	Oxine Dithizone
		Zirconium	Phenylarsonic acid

[22] A new impetus to work in this field was given by F. Feigl's systematic discussion of the organic functional groupings that tend to make reagents more specific; Feigl's views are summarized in his book, "Qualitative Analyse mit Hilfe von Tüpfelreak-

Reagents.—*Aluminon.*—Ammonium salt of aurin tricarboxylic acid· $C_{22}H_{23}O_9N_3$, Mol. Wt. 473.42. A 0.1% solution of the substance in water is used as reagent. The lake is formed in faintly acid solution (acetic acid acetate buffer) then ammonia and ammonium carbonate are added. Iron and phosphate should be absent. Beryllium gives a lake similar to the red one formed by aluminum. See the Chapter on Aluminum.[23]

Benzidine.—Benzidine hydrochloride is added to the neutral or slightly acid solution of the sulfate; the precipitate is filtered, washed with water and the moist precipitate is suspended in water and the sulfuric acid liberated by hydrolysis at 50° is titrated with sodium hydroxide. For details see Chapter on Sulfur; also Chapter on Water Analysis (Vol. II).

α-Benzoin Oxime.—Dissolve 2 g. of the reagent in 100 ml. of alcohol. In ammoniacal tartrate solution the reagent separates copper from Co, Ni, Fe, Al, Pb; the precipitate $Cu(C_{14}H_{11}O_2N)$ contains 22.01% Cu if dried at 110° C. In acid solution the reagent precipitates only Mo^{VI}, W, Pd, Cr^{VI}, V^V and Ta. Chromium and vanadium do not interfere if reduced to the tri- and quadrivalent states, respectively. A solution containing 5% of sulfuric acid by volume is preferable. The molybdenum precipitate is carefully charred while moist in a platinum crucible, and the oxide, MoO_3, is brought to constant weight after heating at 500–525° C. in a muffle. (See Molybdenum Chapter for Procedure.) [24]

Copper is precipitated from hot ammoniacal solution. A maximum of about 0.05 g. of copper should be present and 10 ml. of reagent (0.2 g.) should be required. The voluminous green precipitate is collected on a weighed filtering crucible, washed thoroughly with hot 1% ammonia and finally with 2 or 3 small portions of hot alcohol to remove any excess of reagent. The precipitate is dried to constant weight at 110° C.

Cupferron.—Ammonium β-nitrosophenylhydroxylamine. $C_6H_5N(NO)ONH_4$, Mol. Wt. 155.15. The aqueous solution of the reagent is not very stable; it is best to use a fresh cold 5 or 6% solution. (The solution rapidly darkens, but may be used for precipitations for a few days after its preparation.) The reagent is not a specific one, for it gives quantitative or substantial precipitations of the following in acid solutions: Cu, Ag, Pb, Hg, Sn, Fe^{III}, Ti, Zr, V^V, Cb, Ta, U^{VI}, Th, Ce, W. Arsenic and antimony are partially precipitated if trivalent, but not if quinquivalent. In general the reagent is useful for certain separations, or for determinations after preliminary separations. The precipitates can not be weighed directly, but must be transferred to the corresponding oxides by cautious ignition at the proper temperature.

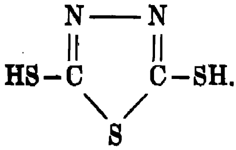
The chief uses of cupferron are: The separation of iron and other precipitable ions from Al, Cr, Mn, Ni, Zn and phosphoric acid; separation of V^V from U^{VI}; separation of Cb and Ta from other substances; the determination of any precipitable element after the preliminary separations have been made.

tionen," 2nd ed., J. Springer, 1935. Also Ind. Eng. Chem., Anal. Ed., **8**, 401 (1936). For systematic reviews of the properties of organic reagents see: "Organic Reagents for Metals," by the staff of Hopkin and Williams, Ltd., London, 1938; and for summaries with literature references: W. E. White, et al., Lange's Handbook of Chemistry; also John H. Yoe, Chemical Rubber Co. Handbook.

[23] Hammett and Sottery, J. Am. Chem. Soc., **47**, 142 (1925); Yoe, ibid., **54**, 1022 (1932); Cox, Schwartz, Hann and Unangst, Ind. Eng. Chem., Anal. Ed., **24**, 403 (1932).

[24] H. B. Knowles, J. Research Natl. Bur. Standards, **9**, 1 (1932).

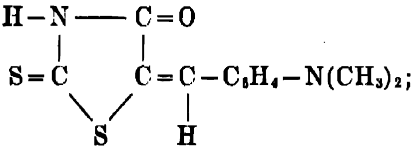
Dimercaptothiodiazol.—The reagent is prepared by the interaction of carbon disulfide and hydrazine hydrate:



It is non-specific, but very sensitive for bismuth, copper and lead. Dissolve 0.7 g. in 35 ml. of 0.1 N KOH for use as a reagent.[25]

p-Dimethylaminobenzylidenerhodanine.—The best solvent for the reagent is acetone. Silver, cuprous, mercury, gold, platinum and palladium solutions give precipitates with the reagent.[26]

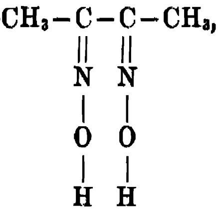
Formula:



; Mol. wt. 264.35.[26]

A 0.03 g. per 100 ml. solution is used. The reagent is useful for the colorimetric determination of traces of silver. Soft glass should not be used for extremely dilute silver solutions (about 1 p.p.m.) because of adsorption of Ag^+ by the vessel.

Dimethylglyoxime.—



, Mol. wt. 116.12.

Nickel is the only element that gives a definite weighable compound with the reagent, $Ni(C_4H_7N_2O_2)_2$; palladium may be precipitated quantitatively by the reagent, but the precipitate must be ignited to give the metal. Bismuth, cobalt and certain other ions give delicate color reactions with the reagent. A 1 or 2% solution of the compound in hot alcohol is used as reagent. For details see chapter on Nickel.

Diphenylaminesulfonic Acid.—Mix 0.512 g. of the barium salt in 125 ml. water with 0.117 g. of anhydrous Na_2SO_4 in a little water. Filter off the barium sulfate and dilute the filtrate to 250 ml. The solution is 0.006 M. Unknown and standard nitrate solutions should contain from 0.1–5 mg. nitrate and 10 g. KCl per liter. To 10 ml. of nitrate-KCl solution is added 10 ml. concentrated H_2SO_4 and after cooling, 0.1 ml. of 0.006 M sodium diphenylamine sulfonate. The colors are compared. The procedure is empirical and is a test for oxidizing power. A pretreatment of the solution to be tested with ammonium chloride is necessary if nitrite is present. A 100 ml. sample of solution plus 0.5 g. NH_4Cl is boiled down to 25 ml. and made up to the original volume after adding 0.5 g. KCl.[27]

[25] Dubsky and Okáč, Z. anal. Chem., 96, 267 (1934).

[26] Feigl, Krumholz and Rajmann, Mikrochem., 9, 165 (1931); Kolthoff, J. Am. Chem. Soc., 52, 2222 (1930); Schoonover, J. Research Natl. Bur. Standards, 15, 377 (1935).

[27] Kolthoff and Noponen, J. Am. Chem. Soc., 55, 1448 (1933).

Diphenylcarbazide.—Dissolve 0.2 g. of the compound in 10 ml. of glacial acetic acid and dilute to 100 ml. with 95% alcohol. The reagent is unstable and should be prepared daily or every few days (latter for Cr test). For chromate, 25 ml. of the solution to be tested is treated with 2 ml. of the reagent. If the chromate solution contains a slight amount of acetic acid, as little as 1 part of chromate in 71×10^6 parts of solution can be detected. The color is violet for small amounts and reddish for large. Cadmium, copper and mercury give similar colors in neutral solution.[28]

Dithizone.—Diphenylthiocarbazone. $C{=}S\begin{array}{l}\nearrow N{=}N{-}C_6H_5\\ \searrow NH{-}NH{-}C_6H_5\end{array}$. Mol. wt. 256.32. Stock solution: 0.1 g. dithizone in 100 ml. of chloroform. The reagent may be used for the sensitive detection of Pb, Zn, Hg, Ag, Sn, Cd, Cu, Co, Ni, Mn, Tl, Bi. Only Pb, Tl and Bi are extracted from an ammoniacal cyanide solution by the reagent. (See Chapter on Lead.) In the absence of interfering ions the reagent is very sensitive for zinc.[29]

Dipicrylamine.—Hexanitrodiphenylamine. Mol. wt. 439.22. The reagent forms slightly soluble salts with K, Rb and Cs, but not with Li, Na, Mg and Ca. The ammonium salt is more soluble than the potassium salt. The magnesium or the sodium salt of dipicrylamine is used as reagent. In the presence of very large quantities of sodium the potassium salt must be dissolved and reprecipitated.[30]

Preparation of the Reagent.—The commercial ammonium salt is dissolved in hot water, filtered, and the free acid is precipitated with sulfuric acid filtered and washed. The yellow free acid is heated with an aqueous suspension of magnesium carbonate, and the dark red solution is filtered and converted into the sodium salt with concentrated salt solution. Fifty grams of the sodium salt are dissolved in 10 liters of water, impurities allowed to settle, and the free acid is again precipitated by dil. sulfuric acid. The acid is converted into the sodium or magnesium salt of 0.2 to 0.5 N concentration. (Mol. wts. $NaC_{12}H_4O_{12}N_7 = 462.2$; $Mg(C_{12}H_4O_{12}N_7)_2 = 900.73$). *Determination:* The potassium solution should be neutral; a 25% excess of reagent should be added. The precipitate is collected on a Jena G 4 filtering crucible, transferring the last traces of precipitate to the crucible with ice-cold distilled water, and the precipitate is washed once with the latter, then with a solution of the potassium salt (0.5 g. of $KC_{12}H_4O_{12}N_7$ per liter). Finally it is washed once more with a little ice water, then dried at 100° C. for 1 hour. The weight of ppt. $\times 0.08191$ gives weight of potassium found.

NOTES.—If the potassium solution contains phosphate the sodium reagent rather than the magnesium one must be used.

Sulfates do not interfere.

The reagent is recovered as follows: The potassium salt is dissolved in acetone, and the free acid is precipitated by adding sulfuric acid (dilute). The precipitate is washed, and transposed into the sodium or the magnesium reagent of proper concentration (0.2 to 0.5 N).

[28] Stover, J. Am. Chem. Soc., 50, 2363 (1928); Scott, ibid., 51, 3351 (1929); Kolthoff, Chem. Weekblad., 21, 20 (1924); Tougarinoff, Ann. Soc. Sci. Bruxelles, 50, B, 164 (1930) through C. A., 25, 1456 (1931).

[29] Hibbard, Ind. Eng. Chem., Anal. Ed. 9, 127 (1937).

[30] Winkel and Maas, Angew. Chem., 49, 827 (1936).

8-Hydroxyquinoline.—See Oxine.

Nitron.—Diphenylendoanilohydrotriazole, $C_{20}H_{16}N_4$. Forms nitron nitrate, $C_{20}H_{16}N_4 \cdot HNO_3$, containing 16.52% NO_3. A 10% solution of nitron in 0.1 N acetic acid is used. 10–12 ml. of the reagent will precipitate 0.1 g. of nitrate. The reagent also precipitates perrhenate and may be used for the quantitative estimation of rhenium.

α-Nitroso β-Naphthol.—A saturated solution of the reagent in 50% acetic acid is used. For 100 ml. of solution 2 g. of reagent are added to 100 ml. of hot 50% acid, and the undissolved excess is filtered off after cooling the solution. This quantity of reagent is required per 0.1 g. of cobalt. Palladium, iron and copper also react with the reagent.

Oxine. 8-Hydroxyquinoline. Orthohydroxyquinoline.—Triturate 2.5 g. of the reagent with 5 ml. of glacial acetic acid and made up to 100 ml. with hot water. After cooling and filtering the reagent is 0.15–0.2 M; 1 ml. of it should precipitate about 1.5 mg. of Al; 2.25 mg. of Mg, etc.

The reagent is used at present primarily for separation and determination of Al, Be, Mg, Zn, Cd and Bi, but it is non-specific and precipitates many other ions under various conditions. In mineral acid solutions no ions are precipitated by the reagent. In acetic acid-acetate buffer the reagent precipitates: Bi, Cd, Cu, Al and Zn. (Also precipitated in acetic acid solution: Ag, Pb, Hg(ic), $Sb^{III \text{ or } V}$, Fe(ous or -ic), Ti, Zr, Mn, Co, Ni, U, V, Ta, Cb.) In ammoniacal and in sodium hydroxide solution nearly all of the elements that are precipitated in acid solution are also insoluble, and in addition Mg, Be, Ca, Sr, Ba etc. are precipitated. The reagent is very useful in the separation of Al from Be or Mg. In ammoniacal solution or in ammoniacal peroxide solution Al may be separated from phosphate, pervanadate, permolybdate, pertitanate, pertantalate, percolumbate, arsenate, fluoride and borate.)[31]

Phenylarsonic Acid, Propylarsonic Acid.—These substances are almost specific reagents for zirconium under certain conditions.[32] Propyl arsonic acid is suitable for the determination of zirconium in the presence of tin, thorium and titanium. The solution should contain 10% of concentrated HCl by volume or 4.5% of concentrated H_2SO_4. Antimony and bismuth interfere. The zirconium is weighed as ZrO_2. A 5% aqueous solution of the reagent is used.

Phenylthiohydantoic Acid.—The reagent is soluble to the extent of about 1% in water or alcohol at 20° C. About 10 g. dissolve in 100 ml. of water at 100° C. The reagent is much more soluble in acetone than in alcohol or water. From a hot slightly ammoniacal solution the reagent separates cobalt quantitatively in one operation from As, U, V, Ti, W, Mo, Zn, Mn, Cr, Al, Mg and Ca. Citrate may be present to hold iron, etc. in solution. From 1–5 mg. of iron and part of any nickel present will be found with the cobalt precipitate. In solutions slightly acidified with acetic acid the reagent precipitates Cu, Pb, Hg, Cd, Bi, Sb quantitatively while Sn, As, and metals not in the H_2S group are not precipitated. The compositions of the precipitates are variable so that each

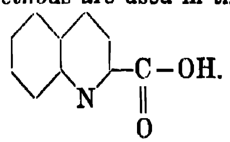
[31] For details see Lundell and Knowles, J. Research Natl. Bur. Standards, 3, 91 (1929).

[32] Rice, Fogg and James, J. Am. Chem. Soc., 48, 895 (1926); Klinger, Tech. Mitt. Krupp, 3, 1 (1935) through C. A. *n*-propyl arsonic acid—Arnold and Chandlee, J. Am. Chem. Soc., 57, 8 (1935).

metal must be determined by some standard volumetric or gravimetric process after destroying the organic matter.[33]

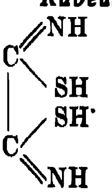
Phenyltrimethylammonium Iodide.—Cadmium, in neutral or slightly acid solution gives a white crystalline with potassium iodide and the reagent of composition $[C_6H_5(CH)_3N]_2CdI_4$. A 2.5% aqueous reagent is used.[34] Other hydrogen sulfide group metals should be removed by reduction with metallic iron. Before precipitation the solution is treated with a few drops of sulfurous acid and an excess (5 g.) of Rochelle salt, and potassium iodide (2–3 g.). After standing at least 6 hrs. the precipitate is collected on a filtering crucible, washed with small portions of a solution containing both KI (0.5%) and phenyltrimethylammonium iodide (0.5%). The precipitate is dissolved in 2 N ammonia, neutralized and made 1 N in HCl and titrated with potassium iodate after adding 5 ml. of 10% KCN solution and starch indicator. When the iodide of the precipitate has been converted into iodine cyanide the starch end-point (blue to colorless) appears. One ml. of M/40 $KIO_3 = 0.001405$ g. Cd. since $2KIO_3 = 4I^- = Cd$.

Picrolonic Acid (1-pNitrophenyl-3-Methyl-4-Nitro Pyrazolone). The reagent is soluble in water or alcohol. A 2.5–2.64 g./l. aqueous solution is used as reagent. The elements determinable are Cu, Pb, Ca, Mg and Th. Precipitates of the composition $M^{II}(C_{10}H_7O_5N_4)_2 \cdot nH_2O$, are formed.[35] Gravimetric, colorimetric and titration methods are used in the final measurement.

Quinaldinic Acid.—$C_{10}H_7NO_2$ or  Chief use: Separation of zinc from Fe, Al, Ti, Cr, Be, UO_2 in alkaline tartrate solution; separation of copper from Cd, Mn, Ni, Co etc. The zinc is weighed in the form of $Zn(C_{10}H_6O_2N)_2 \cdot H_2O$ after drying at 105° C.[36]

Quinalizarin.—(1,2,5,8 Tetrahydroxyanthraquinone.) For color tests or colorimetric determination of Be, Al, etc. a 0.05% solution of the dye in 0.25 N NaOH or an alcoholic solution is used. For details see Chapters on Aluminum and Beryllium. Beryllium may be detected in the presence of magnesium since the complex of the latter with the reagent is readily oxidized by bromine. Zr, Ce, Th, La, etc. (rare earths) give a reaction analogous to that of beryllium —blue in alkaline solution.

Rubeanic Acid, NH_2-CS-CS-NH_2, which appears to react in the imid form,



A saturated solution of the compound in alcohol is used as the

[33] Willard and Hall, J. Am. Chem. Soc., **44**, 2219, 2226, 2237, 2253 (1922).

[34] Pass and Ward, Analyst, **58**, 667 (1933).

[35] For Pb: See Hecht, et al., Z. anal. Chem., **95**, 152 (1933); Ca, See Alten, et al., Biochem. Z., **265**, 85 (1923); Bottiger, C. A., **29**, 7857 (1935); Mg, See Bottiger, ibid., **29**, 7859 (1935); Th, See Hecht and Ehrmann, Z. anal. Chem., **100**, 87 (1935).

[36] Ray, et al., Mikrochemie, **17**, 11, 14 (1935); **18**, 89 (1935); Z. anal. Chem., **100**, 324 (1935).

reagent. The compounds of the substance and the ions of copper, lead, cobalt, nickel and the platinum metals (Ru, Pd, Pt) may be detected and estimated colorimetrically under proper conditions. Silver and mercurous ions also give reactions (black precipitates; sulfides?).[37]

Salicylaldoxime,[38] ***C_6H_4 (OH)CHNOH.***—A 1% solution in 5% alcohol is used, the substance first being dissolved in the alcohol and diluted. Copper is precipitated by the reagent in a solution containing 10% of glacial acetic acid; Ni and Co are precipitated from neutral solution and lead from neutral or alkaline solution. The compounds $Cu(C_7H_6O_2N)_2$, $Ni(C_7H_6O_2N)_2$ and $PbC_7H_6O_2N$ may be dried at 100° and weighed. Alternatively the precipitates may be dissolved in sulfuric acid, decomposed by heating in the presence of excess ferric sulfate and the ferrous sulfate that is formed may be titrated.

Thionalide.—*β*-Aminonaphthalide, $C_{10}H_7NHCOCH_2SH$. The compound is only slightly soluble in water (0.08 g. per 100 ml. at 95° and 0.01 at 20° C.). It is readily soluble in C_2H_5OH, glacial acetic acid or concentrated H_2SO_4; on warming the last solution decomposes. In 0.2 N nitric or sulfuric acid Cu, Ag, Au, Hg, Sn, As, Sb, Bi, Pt and Pd give precipitates. The following precipitate in alkaline tartrate solution: Cu, Ag, Au, Hg, Cd, Tl, Mn, Fe (ous); in tartrate-cyanide solution: Au, Tl, Sn, Pb, Sb, Bi; and in NaOH-KCN solution: Tl, Hg, Pb, Bi. The precipitates may be weighed after drying at 105° C. The reagent may be titrated:

$$2C_{10}H_7NHCOCH_2SH + I_2 = (C_{10}H_7NHCOCH_2S)_2 + 2HI.$$

Triphenyltinchloride.—Reagent for fluorine; see chapter on Fluorine.

[37] Ray, Z. anal. Chem., **79**, 94 (1929); Feigl, Mikrochemie, **8**, 239 (1930); also "Qualitative Analyse mit Hilfe von Tüpfelreaktionen." Wölbing and Steiger, Mikrochemie, **15**, 295 (1934).

[38] Copper: Ephraim, Ber., **63**, 1928 (1930); **64**, B, 1210, 2819 (1931); Reif, Z. anal. Chem., **88**, 38 (1932). Cu and Ni: Astin and Riley, J. Chem. Soc. (Lond.), 314 (1933). Cu: Hecht and Reissner, Mikrochemie, **17**, 127 (1935); Ishibashi and Kishi, J. Chem. Soc. Japan, **55**, 1060, 1065, 1067 (1934). Pb: Ishibashi and Kishi, Bull. Chem. Soc. (Japan), **10**, 362 (1935). Tougarinoff, Ann. Soc. Sci. Bruxelles, **54B**, 314 (1934).

STANDARD LABORATORY APPARATUS[1]

VOLUMETRIC APPARATUS

Very great advances have been made in the United States toward the standardization of volumetric apparatus, first by the U. S. Bureau of Standards and more recently by a committee representing manufacturing chemists. The latter, in cooperation with the manufacturers and dealers of chemical apparatus, has completed its recommendations for the standardization of several types of volumetric glassware, in regard to types, quality, design, workmanship and units of capacity. This is a commendable advance but while it will insure a supply of standard volumetric glassware, if the movement is generally supported by both makers and users, it does not preclude the necessity of recalibration or verification by the chemist himself. This is especially evident when we recall the fact that volumetric chemical analyses are often reliably calculated to 0.01%, whereas the volumetric glassware may be in error to such an extent as to make the 0.10% figure unreliable.

The following principles, procedures and tables for testing and calibrating volumetric apparatus, except for a few additions, were obtained from publications of the U. S. Bureau of Standards.

Preparation of Apparatus.—Having selected standard apparatus, it should be thoroughly prepared for calibration by removing all foreign material, dirt, grease, etc., from the surface by one of the following methods:

1. By immersion for several hours in a concentrated solution of caustic soda in 95% alcohol, after which it should be washed with sulfuric acid and water and allowed to drain until dry.

2. By immersion in fuming sulfuric acid for a few minutes, washing with water, then with caustic soda solution and finally with water and allowing to drain until dry.

3. Concentrated sulfuric acid saturated with chromic acid is a very efficient cleaning solution. This may be substituted for the fuming sulfuric acid in the above procedure.

4. Another method by which small apparatus, such as flasks, burettes, pipettes, etc., may be quickly and thoroughly cleaned but with which great precaution should be exercised is as follows: To two volumes (10–20 ml.) of 95% alcohol in the apparatus add one volume (5–10 ml.) of concentrated nitric acid. This mixture develops a rather violent action in from one to five minutes, generates much heat and thoroughly cleans the surface with which it comes in contact. This mixture should be used very cautiously and sparingly and should not be confined. The action is accelerated by warming and is almost explosive at times. The change in volume of the apparatus and thermal hysteresis due to the heating by this method of cleaning can usually be neglected if a sufficient drainage and cooling period is employed.

Stopcock Grease.—Soft grease. Thoroughly mix, by melting and stirring, three parts of vaseline and one part of beeswax.

[1] Contributed by R. M. Meiklejohn and J. S. Coye.

Hard grease. Add one part (i.e., 1 : 4) of soft black rubber in small bits to the above mixture, heat to 140–150° C., and stir constantly until thoroughly incorporated.

Measurement of Capacity.—There are two general methods in use by which the capacity of an apparatus is determined, the choice being determined by the character of the apparatus; namely, direct measurement and calculation of capacity from the weight of water which it contains or delivers.

Direct Measurement.—This method is especially applicable to the testing or calibration of flasks and consists in allowing water at a constant temperature

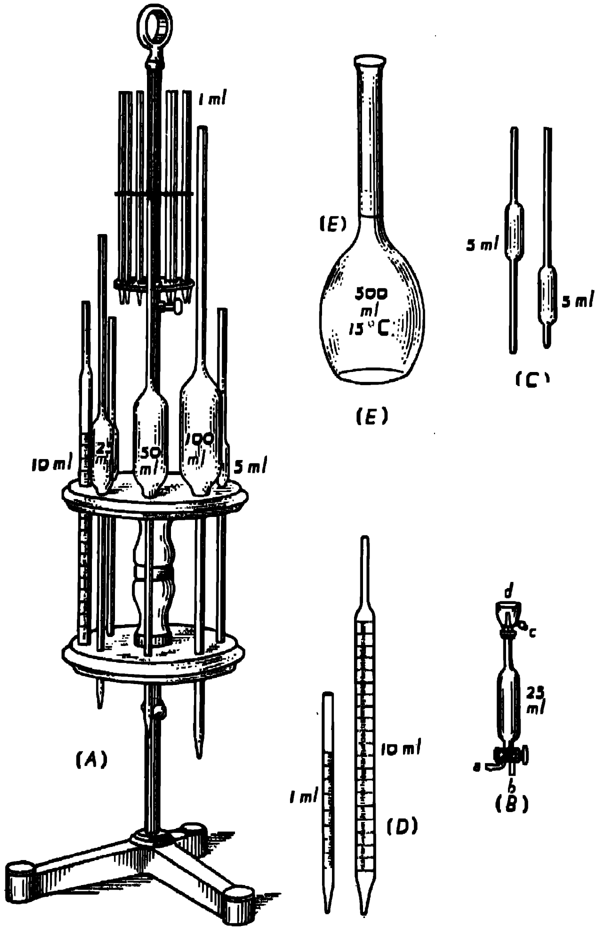


FIG. 129. Volumetric Measuring Apparatus.

to flow from a standard pipette, which is graduated at the lower end, into the flask at a rate of flow standard for the pipette until the flask is filled to its graduation mark. The volume (capacity) of the flask is then read off on the graduation of the standard pipette, making any instrumental correction applying to the standard pipette as determined by the procedure of calculation of capacity at 20° C. from the weight of water delivered under the standard

conditions of outflow. It is evident that this method gives a direct measurement of capacity at the standard temperature of 20° C. regardless of the temperature of water except that the water should be maintained at a constant temperature throughout the entire operation. This change of temperature is the only inherent error in the procedure, except the error of unequal expansion of the two glasses, which is assumed to be negligible. The chief disadvantage in the procedure is that a separate standard pipette is necessary for each size of flask, and consequently is only applicable when a large number of flasks are to be calibrated.

Calculation from Weight of Water.—The quantity sought in this case is the actual volume of water contained or delivered by the apparatus at the standard temperature of 20° C. and is calculated from quantities observed, obtained from tables, and calculated.

Quantities observed.

V = nominal capacity of apparatus (milliliters).
t = temperature of water weighed.
a = apparent weight in air of water.
b = buoyancy constant (Table 1).

Quantities obtained from Tables.

d_t = density of water at t° C. (Table 2).
M = mass of water having a volume V at t° C. (Table 2 $d_t \times V$).
A = apparent weight in air of water having volume V at t° C. (Table 3).

Quantities calculated.

v = volume of water at t° C. (milliliters).
C = capacity of instrument at standard temperature 20° C.

The capacity v at the observed temperature t° C. is first calculated. This may be accomplished by one of three formulae according to the precision desired.

In all cases where the greatest precision is desired the following formula is used.

1. $$v = \frac{a}{d_t + b}.$$

d_t is obtained from a table of water densities.

b may be obtained from tables or may be observed directly as follows: Place a hollow sealed glass bulb of known volume (about 1000 ml.) and mass on one pan of a balance and an equal mass of brass weights on the other pan of the balance. The additional weight w required on the bulb pan for a balance is then the buoyancy of the volume v of the bulb for the atmospheric conditions prevailing, or $b = \frac{w}{v}$ = grams per milliliter. The mass of the bulb is its true weight in vacuum and may be calculated from its apparent weight by adding, to its apparent weight in air, the weight of an equivalent volume of air at the temperature and atmospheric conditions prevailing at the time the apparent weight was obtained minus the weight of a volume of air equal to the volume of brass weights used in obtaining the weight in air.

Example:

Volume displaced by the bulb = 950 ml. = .950 liter = V_b.

Apparent weight of bulb at 22° C. and 740 mm. mercury (corrected to 0° C. and standard gravity) with brass weights = 218.124 gms.

Then $\frac{218.124}{8.4} = 25.95$ ml. = .02595 liter = V_w or volume of brass weights.

Then $218.124 + \frac{(V_b - V_w) \times 1.2930}{1 + .00367 \times t} \times \frac{P}{760}$ = true weight of bulb.

Or $\quad 218.124 + \frac{(.950 - .02595) \times 1.2930}{1 + .00367 \times 22} \times \frac{740}{760} = 219.2005.$

This true weight or mass of the bulb is then the value to be used in determining the buoyancy constant for the particular atmospheric conditions prevailing or

$$\text{buoyancy constant} = \frac{219.2005 - 218.124}{950.} = .001133 \text{ gm.}$$

or 1.133 mgs. per milliliter.

This figure is obtained by assuming the air to be dry and free from carbon dioxide. The value of 1.2930 gms. as the weight of one liter of air at 0° C. and 760 mm. pressure at sea level is obtained only under these conditions and consequently requires corrections for the carbon dioxide and moisture content of the air at the time the weight is taken. For ordinary work Table 1, as prepared by the U. S. Bureau of Standards, gives the buoyancy constant of sufficient accuracy.

When V is a round number, the following approximate formula simplifies the calculation.

2. $v = V + a + (V \times b) - M.$

M = the mass of water having a volume V at $t°$ C. and may be calculated from water density tables. (Table $2d_t \times V$.)

b is obtained as above.

If $v - V$ is less than $1/1000v$, the error will not be greater than $1/200{,}000v$.

When V is a round number and the buoyancy constant is not observed, the following formula may be applied.

3. $v = V + a - A.$

A may be obtained from tables. (Table 3.) The values obtained by this formula are equal in accuracy to those obtained by formula 2.

After calculating v by one of the above formulae, the capacity C of the apparatus at 20° C. is calculated by the formula

$$C = v + .000025\, v\, (20 - t).$$

The value .000025 is taken as the average cubical expansion of glass.

Values for $.000025\, v\, (20 - t)$ have been calculated and tabulated by the U. S. Bureau of Standards.

Flasks.—Flasks are most readily tested or calibrated by direct measurement from a standard pipette as previously described. When the weighing method is employed, the procedure is as follows: The flask is suspended from the left arm of the balance, thus leaving space for weights on the balance pan. A weight somewhat greater than the total weight of the flask when filled to the mark with water is placed on the right balance pan. The clean, dry, empty flask with stopper is then balanced by placing the necessary weights on the pan carrying the flask. The flask is next filled to the mark with water at a definite constant temperature $t°$ C. and again balanced by removing weights. The weights removed give the apparent weight (a) in air of the water at temperature $t°$ C. and p barometric pressure (uncorrected). The capacity C at 20° C. of the flask of nominal volume V is then calculated as previously described.

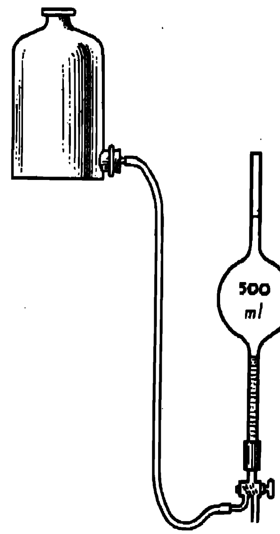


Fig. 130. Morse-Blalock Apparatus in Position for Calibrating Flasks.

Example (500 ml. flask):

$$\begin{array}{rl} & 519.710 \\ & \underline{20.950} \\ a = & 498.760 \text{ apparent weight in air of water at 17° C. and 735 mm.} \\ d_t = & .9988 \text{ density of water at 17° C. (gms. per milliliter).} \\ b = & .001037 \text{ buoyancy constant. (See Table 1.)} \end{array}$$

Then

$$v = \frac{a}{d_t - b} = \frac{498.760}{9988 - .0010} = 499.88 \text{ ml. at } 17° \text{ C.}$$

and

$$C = v + .000025\, v\, (20 - t) = 499.88 + (.000025 \times 499.88 \times 3) = 499.02 \text{ ml. at } 20° \text{ C.}$$

Another procedure of calculating the capacity of a flask from the weight in air of the water contained or delivered which eliminates any error in weighing due to condensation of moisture on the flask is as follows:

A flask of similar type and equal volume is used as the counterpoise on the opposite balance arm when obtaining the weight " a " of water at the temperature of the air.

Then

$$v = \frac{a}{d_t - b} = \text{capacity in ml. at } t° \text{ C.}$$

and

$$C = v + .000025\, V\, (20 - t) = \text{ml. at } 20° \text{ C.}$$

The water used for this work should be pure and freed from dissolved air by previous boiling and should not be allowed to wet the flask above the graduation mark. When filling the flask it should be shaken occasionally to insure complete wetting and removal of any dust, etc., from the glass surface, which might cause the occlusion of minute air bubbles. When possible, these dust particles should be floated off from the top of the water before making up to the graduation mark. If the graduation mark is found to be in error, it may be corrected by making a preliminary mark and subsequently verifying by the above procedure.

Pipette.—Pipettes are most conveniently tested and calibrated by filling once with water at constant temperature t° C. and emptying, then filling again to the mark and emptying into a tared flask. By weighing the flask the apparent weight of water at t° C. delivered is obtained. The capacity of the pipette at 20° C. is then calculated as previously described.

Example:

Standardization of Pipette B-902.

$a = 49.8283 =$ wt. of water delivered at 24.1° C. and 740 mm. pressure.

From Tables 1 and 2:

$b = .00101$ gm.

$d_t = .99732$.

Then

$$V = \frac{a}{d_t - b} = \frac{49.8283}{.99631} = 50.0128 \text{ ml. at } 24.1^\circ \text{ C.}$$

and

$$C = v + .000025 \times V \times (20 - t) = 50.0128 - .005 = 50.008 \text{ ml. at } 20^\circ \text{ C.}$$

The method of draining the pipette should be the same when calibrating as when being used. The most generally accepted method of draining a pipette is to allow it to run out freely until emptied, then the tip is touched against the wetted wall of the vessel into which delivery is being made. The shape and character of the tip and size of the meniscus stem should be as specified by the U. S. Bureau of Standards * and the committee representing the Manufacturing Chemists.†

A pipette may also be calibrated by connecting up with a standard pipette as shown in Fig. 130. The water from the standard is allowed to flow by gravity into the pipette being tested, the standardization being conducted at 20° C.

Burettes.—Type, design, size, etc., of burettes have been standardized by the U. S. Bureau of Standards and the committee representing the chemical manufacturers to such an extent as to make the calibration of them simple and reliable. These specifications are such as to give the proper rate of out-flow to make the residue and after-flow negligible when calibrated under conditions of out-flow indicated for each particular type of burette.

*Committee on Apparatus Standardization of the Manufacturing Chemists' Association of the U. S.

† Scientific Papers No. 92 and Circular No. 19.

In calibrating a burette, the weight of water at constant temperature and pressure which is delivered under standard conditions of out-flow is determined for each graduation of the burette as desired, always beginning at the zero graduation each time. The volume of water for each increment is then cal-

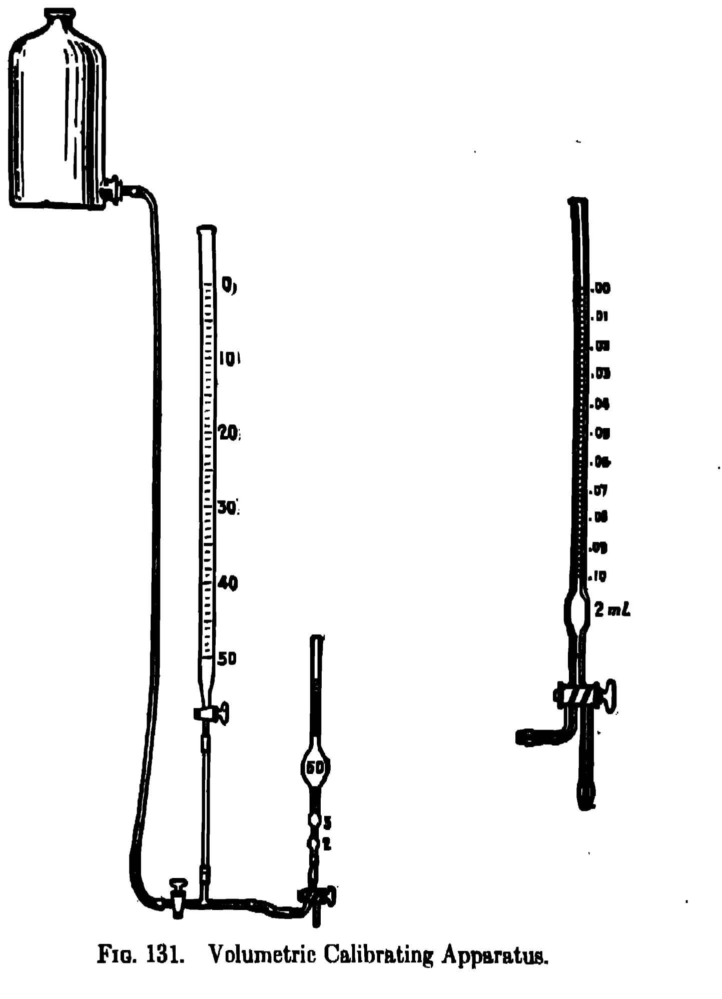


FIG. 131. Volumetric Calibrating Apparatus.

culated as previously described. It is very important that the burette types which have been specified by the standardization committee be selected for calibration.

Example:

Standardization of Burette 1394.

Each increment is weighed and the weight, temperature and pressure recorded, d_t and b obtained from Tables 1 and 2 and the formula $v=\frac{a}{d_t-b}$ and

$C = vt\ .000025 \times V \times (20 - t)$ applied to each increment. The results may be tabulated as follows:

Point	*a*	*C*	*Error*
5 ml.	4.9562	4.98	−.02
10 ml.	9.9463	9.99	−.01
15 ml.	14.9220	14.98	−.02
20 ml.	19.9158	20.00	−.00
25 ml.	24.9019	25.00	−.00
30 ml.	29.8572	29.98	−.02
35 ml.	34.8254	34.96	−.04
40 ml.	39.8001	39.96	−.04
45 ml.	44.8419	45.02	+.02
50 ml.	49.7809	49.99	−.01

A burette may be standardized against a second standard burette or pipette by filling the one to be tested with water (20° C.) and after connecting to the standard allowing the water to flow into the standard. The connections should be filled with water (free from air bubbles) and the water should stand at the 0 point in the measuring apparatus. See Fig. 131. The upper mark of the measuring standard should be below the level of the lowest mark of the vessel being tested. A two-way stopcock makes it possible to empty the measuring standard, the total capacity of which may be only a fraction of that of the burette to be tested.

TABLE 1

Buoyancy Constants (mg./ml.)

Difference in milligrams between the mass and the apparent weight of one milliliter of water weighed with brass weights ($d = 8.4$) in air at various temperatures and barometer readings (unreduced). A humidity of 50% saturation is assumed. To find the weight of one milliliter of air under the conditions assumed in this table, multiply the buoyancy constant by 1.135 (42/37).

Pressure	Temperature in Degrees Centigrade			
	15	20	25	30
640	0.904	0.886	0.869	0.852
650	0.918	0.900	0.883	0.866
660	0.932	0.914	0.897	0.879
670	0.946	0.928	0.911	0.893
680	0.960	0.942	0.924	0.906
690	0.975	0.956	0.938	0.920
700	0.989	0.970	0.952	0.933
705	0.996	0.977	0.958	0.940
710	1.003	0.984	0.965	0.947
715	1.010	0.991	0.972	0.953
720	1.017	0.998	0.979	0.960
725	1.024	1.004	0.985	0.967
730	1.031	1.011	0.992	0.973
735	1.038	1.018	0.999	0.980
740	1.045	1.025	1.006	0.987
745	1.052	1.032	1.013	0.994
750	1.059	1.039	1.020	1.000
755	1.067	1.046	1.027	1.007
760	1.074	1.053	1.034	1.014
765	1.081	1.060	1.040	1.020
770	1.088	1.067	1.047	1.027
775	1.095	1.074	1.054	1.034
780	1.102	1.081	1.061	1.041

TABLE 2

DENSITY (IN GMS. PER MILLILITER) OF WATER AT TEMPERATURES FROM 0° TO 102° C.

Temp. ° C.	Density	Temp. ° C.	Density	Temp. ° C.	Density
0	0.99987	35	0.99406	70	0.97781
1	0.99993	36	0.99371	71	0.97723
2	0.99997	37	0.99336	72	0.97666
3	0.99999	38	0.99299	73	0.97607
4	1.00000	39	0.99262	74	0.97548
5	0.99999	40	0.99224	75	0.97489
6	0.99997	41	0.99186	76	0.97428
7	0.99993	42	0.99147	77	0.97368
8	0.99988	43	0.99107	78	0.97307
9	0.99981	44	0.99066	79	0.97245
10	0.99973	45	0.99024	80	0.97183
11	0.99963	46	0.98982	81	0.97120
12	0.99952	47	0.98940	82	0.97057
13	0.99940	48	0.98896	83	0.96994
14	0.99927	49	0.98852	84	0.96930
15	0.99913	50	0.98807	85	0.96865
16	0.99897	51	0.98762	86	0.96800
17	0.99880	52	0.98715	87	0.96734
18	0.99862	53	0.98669	88	0.96668
19	0.99843	54	0.98621	89	0.96601
20	0.99823	55	0.98573	90	0.96534
21	0.99802	56	0.98524	91	0.96467
22	0.99780	57	0.98478	92	0.96399
23	0.99756	58	0.98425	93	0.96330
24	0.99732	59	0.98375	94	0.96261
25	0.99707	60	0.98324	95	0.96192
26	0.99681	61	0.98272	96	0.96122
27	0.99654	62	0.98220	97	0.96051
28	0.99626	63	0.98167	98	0.95981
29	0.99597	64	0.98113	99	0.95909
30	0.99567	65	0.98059	100	0.95838
31	0.99537	66	0.98005	101	0.95765
32	0.99505	67	0.97950	102	0.95693
33	0.99473	68	0.97894		
34	0.99440	69	0.97838		
35	0.99406	70	0.97781		

TABLE 3

Apparent Weight (in gms.) of Water in Air

(This table gives the apparent weight, for temperatures between 15° and 30° C., humidity 50%, unreduced barometer reading 76 cm., of certain volumes of water weighed with brass weights. This table is based on the data given in Tables 1 and 2, and may be conveniently employed to determine definite volumes of water for calibrating instruments. The table assumes the air to be at the same temperature as the water.)

Temp. ° C.	2000 ml.	1000 ml.	500 ml.	400 ml.	300 ml.	250 ml.	150 ml.
15	1996.11	998.05	499.03	399.22	299.42	249.51	149.71
16	1995.80	997.90	498.95	399.16	299.37	249.48	149.68
17	1995.48	997.74	498.87	399.10	299.32	249.43	149.66
18	1995.13	997.56	498.78	399.03	299.27	249.39	149.63
19	1994.76	997.38	498.69	398.95	299.21	249.34	149.61
20	1994.36	997.18	498.59	398.87	299.15	249.30	149.58
21	1993.95	996.97	498.49	398.79	299.09	249.24	149.55
22	1993.51	996.76	498.38	398.70	299.03	249.19	149.51
23	1993.06	996.53	498.26	398.61	298.96	249.13	149.48
24	1992.58	996.29	498.15	398.52	298.89	249.07	149.44
25	1992.09	996.04	498.02	398.42	298.81	249.01	149.41
26	1991.57	995.79	497.89	398.31	298.74	248.95	149.37
27	1991.04	995.52	497.76	398.21	298.66	248.88	149.33
28	1990.49	995.24	497.62	398.10	298.57	248.81	149.29
29	1989.92	994.96	497.48	397.98	298.49	248.74	149.24
30	1989.33	994.66	497.33	397.87	298.40	248.67	149.20

Note.—The term milliliter, ml., 1/1000 liter, based on the volume occupied by a kilogram of water at its greatest density, has been adopted by the Bureau of Standards and is frequently found on calibrated apparatus. This form has been used in the section on volumetric apparatus in place of the term cc., generally used throughout this book. Owing to the expansion of water, 1000 grams would occupy a greater volume at room temperature than at 4° C. so that 1 cc. would be less than 1/1000 of this expanded volume. The difference of 1 ml. and 1 cc., under convenient workable temperatures, could not be measured by the ordinary burette, so that for practical purposes the volumes represented by ml. and cc. may be considered the same. This expansion has been taken into consideration in calibration of apparatus, the cc. and the liter being volumes in ratio of 1 : 1000, a relativity demanded in volumetric analysis, so that the terminology is of little importance, provided the apparatus used is thus calibrated.

Editor.

STANDARDIZATION OF WEIGHTS

Precision measurement of mass is the first requisite in accurate analysis. The chemist has at his command instruments for the measurement of mass which by far surpass in accuracy the major operations of his work. This is probably largely responsible for the negligence in the care of the balance and weights too frequently observed in the technical laboratory. It is often the case that the average technical laboratory uses analyses calculated to one decimal place more than warranted by the accuracy of the weights used. Assuming all other operations without error, an analysis made on a 1-gram sample and reported as 98.53% requires a weight accuracy of .0001 gram if the last figure is intended to have any significance.

Laboratories doing accurate analytical or research work should always be in possession of a set of standard weights and these weights should be used only in standardizing those in constant use. Where a large number of balances are used, it is advisable to have two sets of standard weights, a Primary and a Secondary set, each ranging from 100 grams to 1 milligram. The Primary set is used exclusively for checking the Secondary set and is checked annually by the Bureau of Standards at Washington, D. C. The Secondary set is used for standardizing the weights assigned to the various balances. Where balances are used constantly, it is advisable to have the weights checked at least monthly against the Secondary set, and the Secondary likewise checked monthly against the Primary set. While this frequent checking may appear excessive, it is quite inexpensive insurance against errors which cannot easily be detected in any other way.

It is advisable to use one-piece gold-plated weights for the Primary Standard. The type designated Class M by the Bureau of Standards is very satisfactory. Lacquered brass weights are very satisfactory for general use.

The practice frequently observed in chemical laboratories of setting out the weights on the balance plate is very bad. While it expedites weighing, the chance of contaminating and changing the accuracy of the weights more than counterbalances the advantage of speed.

Students are frequently taught that it is not necessary for weights to bear true values so long as they are comparable to one another; that is, to bear true relation to each other. This contention holds good so long as all work done by the chemist is related to his balance. This condition does not exist in the majority of technical laboratories. The chemist frequently uses standard solutions made by use of other balances and for this reason his weighings must be comparable to others in the laboratory. This condition necessitates the standardization of all weights to true values.

Although there are several methods for weighing in use in the various technical laboratories, that of the double swing or vibration is probably the best for standardization of weights.

STANDARDIZATION

There are three methods for standardizing weights:

1. Standardizing the weights to true or absolute values.
2. Standardizing the weights to weigh true or absolute weights.
3. Standardizing the weights to bear true relation to each other.

The procedure followed in the first method is dependent upon the comparative arm lengths of the balance. If the arm lengths are equal, the weights are standardized by direct weighing or balancing on the opposite pans. If unequal, by substitution weighing or having both weights, when placed alternately on the left pan, balance a given mass on the right pan.

The standardization of the weights by the second method is independent of arm length. The weights are standardized by adjusting them so that when they are placed on the right pan they balance the standard weights of a similar denomination placed on the left pan.

In small laboratories where there is but one balance used for fine work, or for students' use, the third method is very satisfactory.

In the first two methods of standardization, each weight is standardized independently.

In all cases of two or more weights of one denomination, the second and third should be marked with one and two dots respectively.

It is, of course, assumed that high-grade balances are used and are thoroughly understood by the chemist, and that in weighing, objects to be weighed are placed on the left pan.

First Method. (Assuming the arm lengths unequal).—It is both convenient and time saving in this work to have an extra set of weights to use as counterpoises.

Place a standard 5 or 10 mgm. weight on the left pan and the 5 or 10 mgm. rider on the right beam. Adjust the weight of the rider until it balances the weight on the left pan when it is located at a point indicating that denomination. Remove both weights. Place the standard 100-gram weight on the left pan and balance it with the counterpoise set. Replace the standard with the 100-gram weight to be standardized and adjust the weight until it balances the counterpoise. Continue in this manner throughout the entire set.

In case the balance arms are equal, the counterpoise set may be dispensed with and the set being standardized placed on the right pan. Of course when weights of absolute value are used on a balance having unequal arm lengths, corrections must be made on all weighings.

Second Method.—This method is the more practical since it is independent of arm length. However weights standardized in this way can only be used on the balance on which they have been standardized.

Place the standard 5 or 10 mgm. weight on the left pan and the 5 or 10 mgm. rider on the right beam, adjust the rider until it balances the weight on the left pan when it is on the point indicating the denomination of that weight. Remove both weights. Place the standard 100 gram weight on the left pan and the 100 gram weight to be standardized on the right pan. Adjust the weight until it balances the standard. Continue with all other weights in the same manner one at a time.

Adjustment of Weights.—Since it is not practical in commercial work to use corrections on weights, they should be adjusted when standardized. In the case of brass weights, by removing the top and either adding or removing granulated aluminum or lead (20–40-mesh) as required, and in the case of platinum fractional weights, fusing on gold shavings cut from foil or wire, if light, or removing platinum with a small file if heavy. When aluminum is used for fractional weights and one is found light, it is advisable to destroy it and replace with another.

When making the adjustment of the brass weight, the weight should be gripped with pieces of heavy linen cloth or chamois skin, never with the fingers. The metal should be added or removed with a pair of tweezers and the weight allowed to stand 15 minutes before final checking. While it is standing other weights may be adjusted. In this way little time is lost.

Third Method.—If the arms of the balance are equal, the weights may be compared with each other. If, however, they are unequal, the method of substitution must be used and another set of weights will be required. In the latter case the counterbalance weights are placed in the left pan and the set being standardized on the right.

The following method assumes the arm lengths equal or practically so:

Place the 5 or 10 mgm. weight on the left pan and the 5 or 10 mgm. rider on the right beam. Adjust the rider with fine emery cloth until it balances the weight when on the point indicating its denomination. Take a 10 mgm. weight from another box for use as a tare and call it T. Place T on the left pan and one of the 10 mgm. weights on the right and balance with the rider if necessary. Record the weight, e.g.,

$$0.01 = T + 0.0001.$$

Replace the weight on the right with the other 10 mgm. weight and again balance.

Record the weight, e.g.,

$$0.01_2 = T + 0.0001.$$

Replace the tare with the 20 mgm. weight and put both 10 mgm. weights on the right pan and balance. Record weights as follows:

$$0.02 = 0.01 + 0.01_2 + 0.0001$$

or

$$0.02 = 2T + 0.0003.$$

Replace the 20 mgm. weight with the 50 mgm. weight and place the 20 mgm. weight and tare on the right pan with the two ten mgm. weights. Balance and record the weights, e.g.,

$$0.05 = 0.02 + 0.01 + 0.01_2 + T + 0.0000$$

or

$$0.05 = 5T + 0.0005.$$

Place the 50 mgm. weight on the right pan and the 100 mgm. weight on the left pan. Balance and record the weight, e.g.,

$$0.10 = 0.05 + 0.02 + 0.01 + 0.01_2 + T - 0.0003$$

or

$$0.10 = 10T + 0.0007.$$

The remaining decigram and gram weights are tested in this manner and the results compiled as follows:

Nominal Value	Value Found on Test	Values Using $T=0.01$	Corrected Using 1.0005 as Std.	Corrections
0.01	$T+0.0001$	0.0101	0 0100	+0.0001
0.01_2	$T+0.0001$	0.0101	0.0100	+0.0001
0.02	$2T+0.0003$	0.0203	0.0200	+0.0003
0.05	$5T+0.0005$	0.0505	0.0500	+0.0005
0.10	$10T+0.0007$	0.1007	0.1001	+0.0006
0.10_2	$10T+0.0006$	0.1006	0.1001	+0.0005
0.20	$20T+0.0007$	0.2007	0.2001	+0.0006
0.50	$50T+0.0004$	0.5004	0.5003	+0.0001
1.00	$100T+0.0005$	1.0005	1.0005	+0.0000
2.00	$200T+0.0006$	2.0006	2.0010	−0.0004
2.00_2	$200T+0.0009$	2.0009	2.0010	−0.0001
etc.				

Effect of Buoyancy.—In making accurate weighings the buoyant effect of air on the weight and mass being weighed must be considered. When the mass being weighed has a specific gravity differing with that of the weights, the buoyancy of the air on the two masses will affect the accuracy of the weighing. Thus the weighing of a 1 gram sample of potassium chloride with brass weights without correction for buoyancy results in an error of .00046 gram or approximately .05%.

The following formula may be used in making this correction for general work carried on under normal conditions:

$$\text{Correct weight} = W + .0012\frac{W}{S} - \frac{W}{S_1},$$

where W = the apparent weight of the object, S and S_1 the specific gravities of the object and weights respectively.

.0012 is the weight of 1 ml. of air at normal laboratory conditions.

The specific gravities of metal generally used in weights are Platinum 21.5, Brass 8.4 and Aluminum 2.7.

Precision and Tolerances of Weights.—The following is a table of the Precision of Corrections and Tolerances of Class S analytical weights issued by the U. S. Bureau of Standards, Washington, D. C. While it is quite evident that the Precision of Correction is beyond the accuracy of a 1/10 mgm. or

even a 1/20 mgm. balance, it is however advisable to standardize the weights to the limit of sensitiveness of the balance.

Denomination	*Tolerance*	*Precision of Correction*
100 grams	0.5 mgm.	0.1 mgm.
50	0.3	0.1
20	0.2	0.1
10	0.15	0.05
5	0.15	0.05
2	0.1	0.05
1	0.1	0.05
500 mgms.	0.05	0.01
200	0.05	0.01
100	0.05	0.01
50	0.03	0.01
20	0.03	0.01
10	0.02	0.01
5	0.02	0.01
2	0.01	0.01
1	0.01	0.01

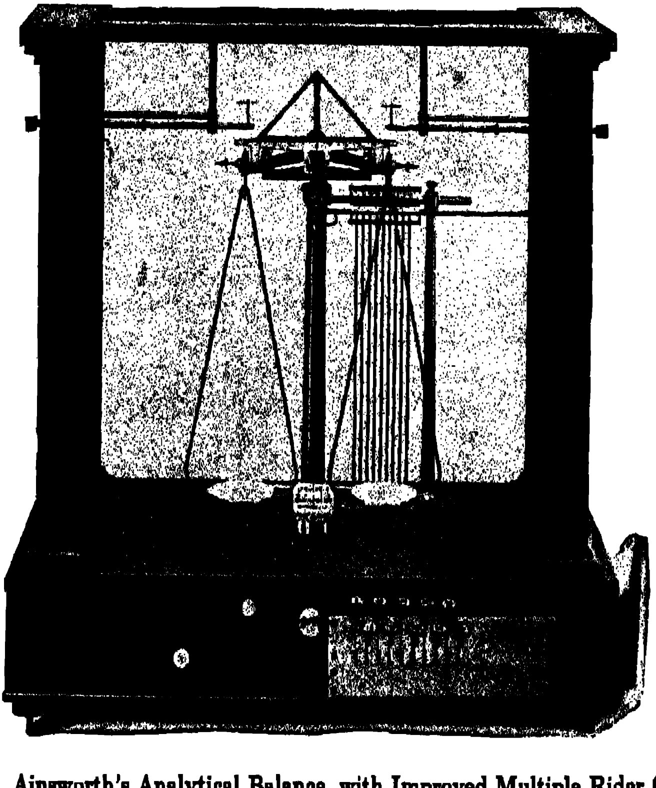


FIG. 132. Ainsworth's Analytical Balance, with Improved Multiple Rider Carrier.

NOTE

The gap in figure numbers and paging between the end of Volume I and the beginning of Volume II, is to allow for the expansion of Volume I, without changing the figure numbers and folios of Volume II.

INDEX TO AUTHORS*

*Page numbers greater than 1300 are in Volume II.
Small Roman numerals in italics refer to the list of authors in Volume II.

N

T

SUBJECT INDEX*

* Pages with numbers greater than 1300 are in Volume II.

G

I

J

M

N

W

SOLUBILITY TABLE

SALT PER 100 ML. OF WATER AT 18° C.

Sr^{++}	Ba^{++}	Ag^{+}	Au^{+++}	Cu^{++}	Mn^{++}	Ni^{++}	Co^{++}	Fe^{++}	Fe^{+++}	Cr^{+++}	V^{++}	Pt^{++++}	Ti^{++++}	Mo^{++++}	W^{++++}	← Cation / Anion ↓
25° .039	25° .121	183.	d	25° .073	25° .186	25° 4.03	25° 1.41	A	.091	W	d	AR	d	d	d	F^-
52.8	35.2	$.0_41$		75.6	18° 197.	64.0	50	41.5	74.4	W	W	AR	d	d	d	Cl^-
98.0	103.	$.0_48$	d	W	127.	130.	4.61	53.5	W	W	—	0.41	d	W	—	Br^-
176.	195.	$.0_63$	d	W	d	59.1	31.0	W	W	W	—	I	W	W	A	I^-
175.	35.5	10 0	d	164.	W	56.7	0° 135.	W	W	W	—	—	—	W	—	ClO_3^-
30.0	0.6	.144	d	W	W	27.6	—	—	—	—	—	—	—	W	—	BrO_3^-
.026	0.02	.004	d	.121	W	1.01	—	—	—	—	—	—	—	—	—	IO_3^-
67.8	8.8	121.0	d	120.	100.	50.	100.	46.0	W	W	—	d	—	A	—	NO_3^-
.004	60.7	1.8	—	7.2	A	16 6	A	A	.023	A	—	—	W	—	—	$C_2H_3O_2^-$
0.78	3.58	.002	A	**	0.9	Alk	A	.0₃6	A	Alk	—	Alk	A	—	—	OH^-
0° 35.0	1.5	.002	A	A	.0₃6	A	A	A	A	A	A	A	I	.106	Alk	O^{--}
d	d	$.0_43$	AR	$.0_43$	$.0_36$	$.0_33$	$.0_34$	$.0_38$	$.0_31$	d	—	A	A	Alk	W	S^{--}
.001	.002	.003	—	.001	.006	.009	A	**	d	**	—	—	—	—	—	
.011	[illegible]	.775	d	19.9	0° 53.7	36.5	15° 32 0	26.4	W	120.	0.80	d	—	W	—	
.004	.008	.003	A	**	.07	A	A	.022	A	A	—	W	—	—	—	
0.12	$.0_22$	.002	—	**	W	A	A	.022	W	A	—	—	—	—		
**	**	.001	—	**	0.02	A	A	A	A							
A	.085	$.0_48$	—	A	A	A	A	A	A							
W	A	$.0_66$	—	I	A	I	I	A	A	A						

References: International Critical Tabl
Inorganic Chem., vol. I–X; Chemiker
A Text-Book of Inorganic Chem., Edit
Seidell, Solubilities of Inorganic and